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Oxidant-Precursor Relationships During Pollutant Transport Conditions. An Outdoor Smog Chamber Study

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Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C Gas Kinetics and Photochemistry Branch

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The analogy between the chemical behavior of chamber simulations and nonurban high-ozone (i.e., 0.08 ppm) systems in the field was good. On the second and third days, the initial charges in the chambers generated ozone concentrations greater than the National Ambient Air Quality Standard for photochemical oxidant (0.08 ppm).

The initial charge of nonmethane hydrocarbon (NMHC) ranged from 1.0 to 10.0 ppmC; nitrogen oxides (NO_x) ranged from 0.100 to 1.000 ppm. Therefore, initial ratios of NMHC/NO_x varied from 7 to 20. On the second and third days in the chambers, concentrations of NO_x ranged from 0.001 to 0.053 ppm; NMHC ranged from 0.53 to 3.78 ppmC. The resulting NMHC/NO_x ratios varied from 16 to 610.

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by

L. A. Ripperton, J. E. Sickles, II, and W. C. Eaton
Systems and Measurements Division
Research Triangle Institute
Research Triangle Park, North Carolina 27709

Contract No. 68-02-1296

Project Officer

J. J. Bufalini
Gas Kinetics and Photochemistry Branch
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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SECTION I

INTRODUCTION

In the troposphere the primary pollutants, nitrogen oxides and hydrocarbons, in the presence of sunlight can serve as ozone precursors. Definition of the influence of various environmental factors (such as transport) on ozone formation is important in the design of strategies to prevent the occurrence of excessive ozone concentrations.

Studies of experimentally produced photochemical smog have been mainly concerned with simulation of "downtown" urban atmospheric conditions. Typically, most experiments have involved from two to six hours of irradiation. Recently observed high nonurban ozone concentrations (greater than 0.08 ppm hourly average) have called attention to the need to study the oxidant/oxidant-precursor relationships in pollution systems after they leave the city (i.e., leave the major sources of pollution). Under these conditions, the pollution system is irradiated for prolonged periods (perhaps for several diurnal cycles) with sunlight and is diluted with nonurban air.

A study designed to investigate this problem should:

1. Determine the influence of oxides of nitrogen/hydrocarbon ratios (NO_x/HC) upon oxidant generation under various conditions of transport (as simulated by different dilution regimes).
2. Determine the potential for oxidant production of NO_x/HC mixtures in the course of several diurnal cycles of irradiation.

The objective of this study is to investigate, in outdoor reaction chambers, the oxidant/HC/NO_x relationships in air mixtures that are similar to those resulting from drift of air pollution systems from urban environs. Specifically, the oxidant/HC/NO_x relationships will be examined under chamber-simulated conditions of atmospheric dilution and repeated diurnal solar irradiation. The study is designed to address the question of the maximum oxidant concentration obtainable from a given initial concentration of precursors on both the initial day of solar irradiation and on subsequent days of irradiation.

SECTION II

CONCLUSIONS

A study was designed to simulate the effects of transport of oxidant and oxidant precursors on ozone (O_3) concentration behavior downwind from urban areas. To perform this simulation, experimental urban photochemical systems were irradiated for three daylight periods with natural sunlight. In most cases, there was a period of dilution of the reactant system to simulate the dilution of urban pollution downwind of the center city. A system of four 27-cubic-meter (950 cubic feet) outdoor smog chambers was used for irradiation of the pollutants. The chambers were fabricated of an aluminum frame covered with Teflon film.

The initial charges consisted of a mixture of hydrocarbons and oxides of nitrogen (NO_x) (20% nitrogen dioxide) in ratios of 7 to 20 and absolute concentrations of 1 to 10 ppmC nonmethane hydrocarbon (NMHC) and 0.100 to 1.000 ppm NO_x. By the second and third day, the measured NMHC concentration range was 0.33 to 3.78 ppmC and the measured NO_x was 0.001 to 0.033 ppm.

The second and third day behavior of O_3 concentrations was remarkably similar to that observed in the field by RTI in rural areas which exceeded the National Ambient Air Quality Standard (NAAQS) for photochemical oxidant.

The conclusions drawn from the study are presented below. 1) Oxides of nitrogen in the 1-5 ppb concentration range (the noise level of current instrumentation) are capable of generating net concentrations of O_3 in excess of the NAAQS in aged photochemical pollution systems; 2) Nonmethane hydrocarbon (largely "unreactive") concentrations only slightly higher than the NAAQS for NMHC (0.24 ppmC) are capable of generating net concentrations of O_3 in excess of the NAAQS for photochemical oxidant; 3) Although the NMHC concentrations are greater than the NMHC NAAQS, this study suggests the possibility that in the downwind drift of the urban plume the current NMHC standard is ineffective to contain the O_3 concentrations below the oxidant standard; 4) The O_3-precursor relationship as indicated by various graphs in the criteria document (ref. 1) do not seem applicable to the second- and third-day irradiation chamber results; 5) Within the chambers aged photochemical systems after a day or two of solar irradiation maintained both O_3-destructive and O_3-generative capacity. This indicates that neither "fossil" O_3 nor local precursor emissions are necessary to produce the O_3 behavior observed in rural high O_3 systems. When "fossil" O_3 and local emissions are present, however, they do influence the nonurban high O_3 systems; 6) "Fossil" O_3 (i.e., O_3 generated in urban areas and retained in air moving downwind from a city) can account for the overnight retention of O_3 concentrations above the NAAQS, but "fossil" O_3 from an urban area cannot be maintained for several days at high concentrations under field conditions without augmenting daytime synthesis; 7) Dilution of a photochemical system producing O_3 does not reduce the maximum O_3 nor the net O_3 concentration in direct proportion to the extent of dilution. At times, the net O_3 generated is greater in the diluted system as compared to an undiluted system, although the maximum may be lower.

SECTION III

RECOMMENDATIONS

Some current problems confronting the planners of oxidant control strategy which can be addressed with smog chamber studies are:

1. Will the achievement of the current NMHC standard in urban areas control O_3 concentrations downwind from the cities?
2. Must one consider total NMHC or only the "reactive" hydrocarbons (e.g., alkenes) to achieve the oxidant standard in nonurban areas?
3. What is the effect of urban pollution on O_3 concentrations in nonurban areas?
4. Given an urban situation in which NMHC is controlled (NMHC NAAQS ~0.24 ppm) and NO_x remains uncontrolled (e.g., NO_x ~0.500 ppm), is there danger of O_3 levels' rising above the NAAQS in areas downwind which have suburban or natural emissions of NMHC and NO_x?
5. What is the O_3-generative capacity of systems containing various NMHC and NO_x concentrations in cold weather (e.g., 4.5°C), especially with multiple-day solar irradiation?

To answer question 1 above, smog chamber studies should extend the range of the initial reactant concentrations to lower levels than are usually employed and react for a 60-hour or greater period.

For example, a study with initial NMHC concentrations of 0.50, 0.25 and 0.10 ppmC (urban mix) would bracket the NAAQS for NMHC. Oxides of nitrogen concentrations of 0.005, 0.010, 0.050, and 0.100 ppm would provide a reasonable range of urban NO_x levels. The initial NMHC/NO_x ratio would be in the range of 1 to 100 (see table 1).

Different dilution rates can be employed to simulate transport of the system out of an urban area. Throughputs, $(\frac{F}{V}t)$, of 0.0, 1.5, and 3.0 in 24 hours will leave ~100%, 23%, and 5% of the original system after dilution. A study with 3 NMHC concentrations, 4 NO_x concentrations, and 3 dilution regimes would provide 36 sets of conditions.

Based on the suggested dilutions and on observations of runs made at concentrations of reactants higher than those listed above, it is evident

Table 1. Initial Reactant Concentrations for a Proposed Extension of the Study of Ozone-Precursor Relationships Under Conditions of Pollutant Transport

NMHC ppmC / NO_x ppm	.10	.25	.50
.005	20	50	100
.010	10	25	50
.050	2	5	10
.100	1	2.5	5

(NMHC/NO_x ratios in the matrix)

that NMHC concentrations on the 2nd and 3rd day would be well below the NAAQS. The downwind urban effects would be well simulated--assuming no additional pollution is added once the air leaves the city.

Question 2 above considers the efficacy of controlling only "reactive" urban hydrocarbons (alkenes) to control oxidant downwind of the city. If one choses conditions using an urban hydrocarbon mix, which upon irradiation bracket the photochemical oxidant NAAQS on the second and third days of the run, the same run could be made with representative alkanes and aromatics instead of the urban hydrocarbon mix. Both single compounds (e.g., isopentane) and a surrogate rural mix (e.g., with 2 or 3% olefins) could be used.

A set of 3 series of experiments could be run to address this problem. Three NMHC concentrations (e.g., 0.5, 0.25, 0.05 ppmC), three NO_x concentrations (e.g., 0.100, 0.050, 0.010 ppm), and three hydrocarbon types (urban mix with alkenes, rural mix, and isopentane) would make a study with 27 sets of conditions. This should answer the question of whether only the reactive hydrocarbons need be controlled to protect areas downwind of the cities from O_3 concentrations above the NAAQS.

Question 3 is basically a question of how urban pollution affects the O_3 concentrations in suburban and rural areas which have some hydrocarbon and NO_x emissions of their own.

Nonmethane hydrocarbon, NO_x, and dilution regimes can be chosen to bracket O_3 production of 0.080 ppm. When dilution begins, a mixture of NMHC and NO_x representative of suburban, small town, or natural conditions can be used as dilution air.

Question 4 is one which has arisen in Los Angeles. Hydrocarbon control without NO_x control has at times resulted in low O_3 concentrations, but with NO_2 concentrations in the middle of the day in the tenths of parts per million range (e.g., 0.500 ppm). A question which arises is what occurs when the urban NO_x is diluted to much lower concentrations with air containing suburban and natural hydrocarbons?

Sets of conditions can be determined in which high concentrations of NO_x (e.g., 0.500 - 1.000 ppm) and low concentrations of NMHC generate no O_3 or only that necessary to satisfy the so-called photostationary condition.

Dilution during irradiation of this system with diluent air containing 0.100 to 0.500 ppm NMHC should put this problem in perspective. Theoretical considerations and practical experience can be used to predict in general terms how the O_3 generation in these systems will behave. The described condition represents a real case, however, and real data from smog chamber runs should answer the question of the desirability of controlling hydrocarbons while leaving NO_x completely uncontrolled.

Question 5 addresses the question of reported winter concentrations of O_3 in excess of the NAAQS in areas north of the Gulf Coast states. The approach to this problem is simple.

Long-range weather forecasts can be consulted to estimate arrival and duration of cold weather (4.5°C) and sunshiny skies. Outdoor smog chamber experiments can then be initiated.

Concentrations of NMHC and NO_x representative of urban areas can be introduced into the chambers and irradiated both statically and in a dilution mode for a series of 3 to 5 sunlight periods.

Initial hydrocabrons could be 0.5, 1.0, and 3.0 ppmC while NO_x concentrations of 0.05, 0.10, and 1.00 could be used. A smog chamber run would represent irradiation of such precursor systems in the cold for several days aloft, away from fresh pollution.

Chamber work is needed to address the problems associated with determining the minimum NO_x which will generate O_3 in concentrations which are at or over the NAAQS, and the circumstances under which this minimum NO_x concentration will produce such high O_3 concentrations. Related is the determination of circumstances under which NO_x or NMHC concentrations are controlling the maximum O_3 accumulation.

To some extent, the studies suggested above will provide information on the problems mentioned in the preceding paragraph. It is felt that the problems of determining the minimum NO_x and NMHC concentrations which can generate O_3 levels in excess of 0.08 ppm would best be approached at this time by studies similar to those recommended for questions 1 through 5 above.

SECTION IV

DESCRIPTION OF RTI SMOG CHAMBER FACILITY

DESIGN

The Research Triangle Institute has constructed four smog chambers (volume: 27 m^3; surface to volume ratio: 1.9 m^{-1}). Figure 1 illustrates the general design. The chambers were built out-of-doors and irradiation is provided by natural sunlight. The walls are 5-mil FEP Teflon film supported by aluminum frames. The floors are 10-mil FEP Teflon film laid over a reflective material (aluminum foil) which serves to raise the light intensity within the chambers and thus compensate for transmission losses through the walls.

Mixing in each chamber is provided by an 0.45-m aluminum fan blade driven by a 185-W motor using a belt-pulley system. Air velocity measurements were made within each chamber. The minimum air velocity was measured to be greater than 0.05 m sec^{-1} within 0.6 m of the floor. Air velocities increased with distance from the walls to a maximum value in excess of 4.0 m sec^{-1} near the moving fan blade.

In addition to the chambers proper, provisions were made for:

1. Ambient air intake purification
2. Reactant injection
3. Instrumented gas analysis
4. Wet chemical gas analysis

A line drawing illustrating the overall system is provided in Figure 2.

The details of the air purification unit are shown in Figure 3. This unit provides for the normal modes of chamber operation: purge, cleanup, and dilution.

During the purge mode, air is supplied by a blower from a 10-m meteorological tower. This air is then drawn through each chamber and exhausted at flow rates up to 0.34 m^3 min^{-1} by three two-stage diaphragm pumps. Purging may also be accomplished at higher flow rates up to 2.3 m^3 min^{-1} by opening a manway in the floor and allowing the tower blower to force air through each chamber.

After completion of the purge, the chambers are closed and air is recirculated through the purification unit. The purification unit contains the following equipment:

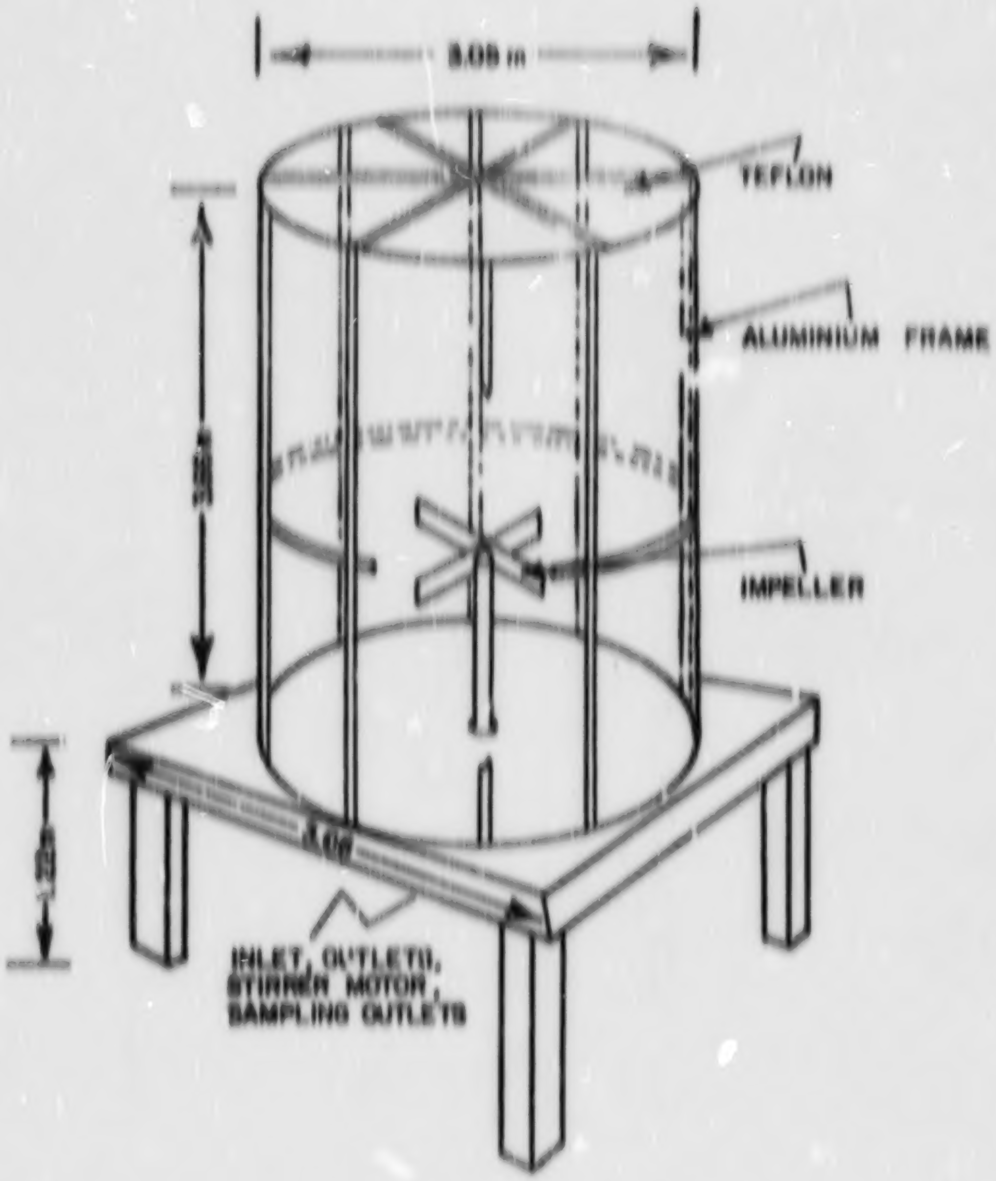
3.05 m
TEFLON
ALUMINIUM FRAME
IMPELLER
INLET, OUTLETS,
STIRRER MOTOR,
SAMPLING OUTLETS

Figure 1. A 27-cubic meter Teflon outdoor smog chamber.

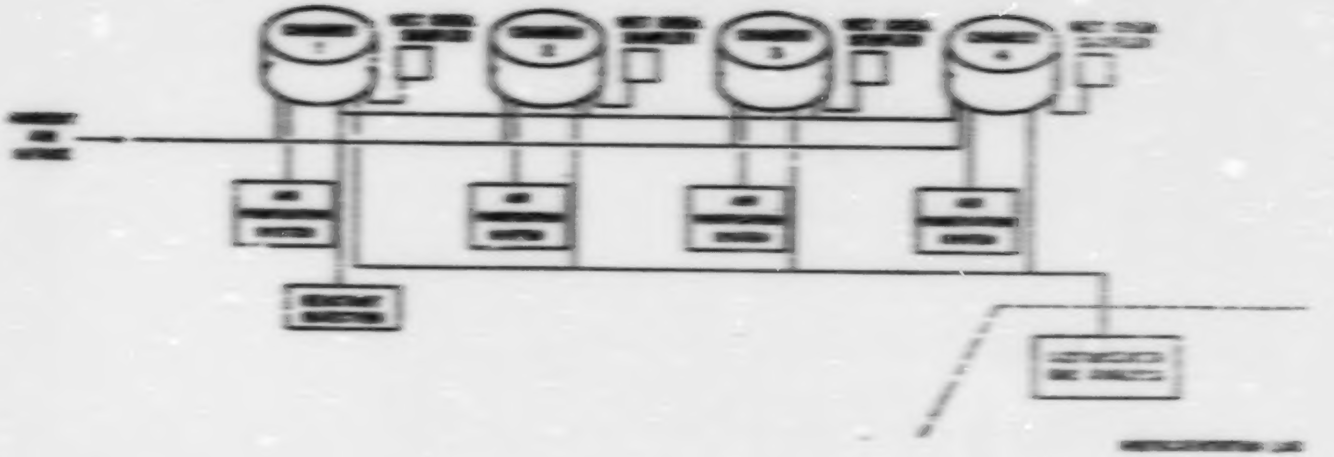

Figure 2. System diagram, [illegible] chambers.

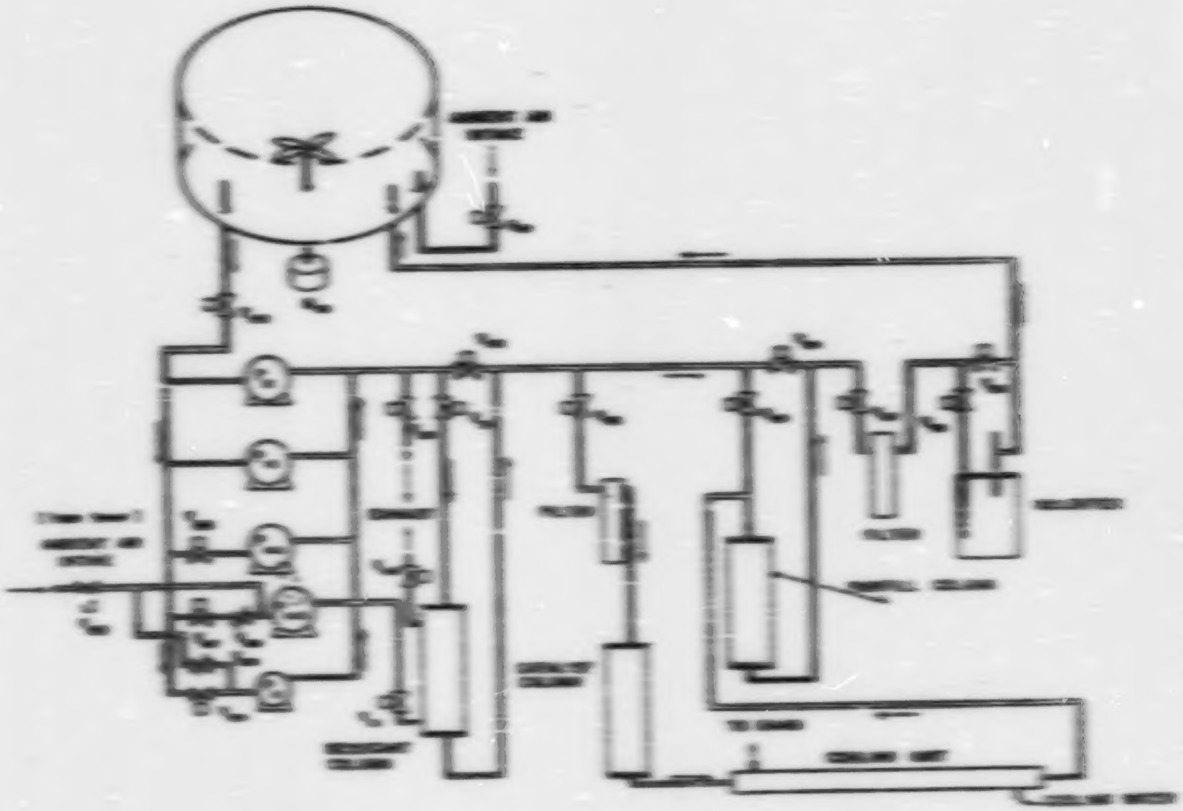

Figure 3. Air purification unit, [illegible] smog chamber.

1. Desiccant column (4A molecular sieves)
2. Two HEPA particle filters
3. Heated catalyst column (0.5% Pt on alumina catalyst; operating temperature: 200-475°C)
4. Air cooler
5. Purafil™ column (for NO_x and O_3 removal)
6. Humidifier

Valving allows the inclusion or exclusion of this equipment as may be appropriate in achieving desired experimental conditions. The purification or "cleanup" operation requires 8 to 12 hours at a flow rate of approximately 0.28 m^3 min^{-1}.

To effect dilution, the chamber contents are recirculated through the purification unit at appropriate flow rates to correspond to the desired dilution rate. Flow rates for this operational mode are between 0.0085 and 0.085 m^3 min^{-1}.

A schematic of the reactant injection system is seen in Figure 4. There are three injection manifolds from cylinders of compressed gases. The flow rates are controlled by calibrated manual needle valves and the quantity of each injection is controlled by timed, manual operation of the appropriate solenoid valves. Hydrocarbons and carbon monoxide are injected sequentially from a single manifold as are NO and NO_2. These manifolds are flushed to ambient between injections by compressed nitrogen. Ozone may be added by injecting oxygen through an O_3 generator to each chamber. A sketch of the sampling system is provided in Figure 5. The samples are drawn sequentially for 10-minute intervals through 0.0048-m ID TFE Teflon™ sample line. An automatic timer activates the appropriate sampling solenoid valves and provides for a 10-minute sample from each chamber once per hour. The remaining 20 minutes are used for instrument calibration or sampling from the ambient air supplied from the tower blower. The sample is drawn at approximately 0.004 m^3 min^{-1} by a Metal-Bellows pump and is supplied to a glass manifold from which the instruments take their samples. These instruments include an O_3 analyzer, a NO-NO_2-NO_x analyzer, an environmental chromatograph, and a dew point sensor. A 1-m-long, 0.0048-m ID TFE Teflon™ tube is located under each chamber. Wet bubbler sampler, condensation nuclei measurements, and bag samples (for detailed HC gas chromatographic analyses) are taken at this location.

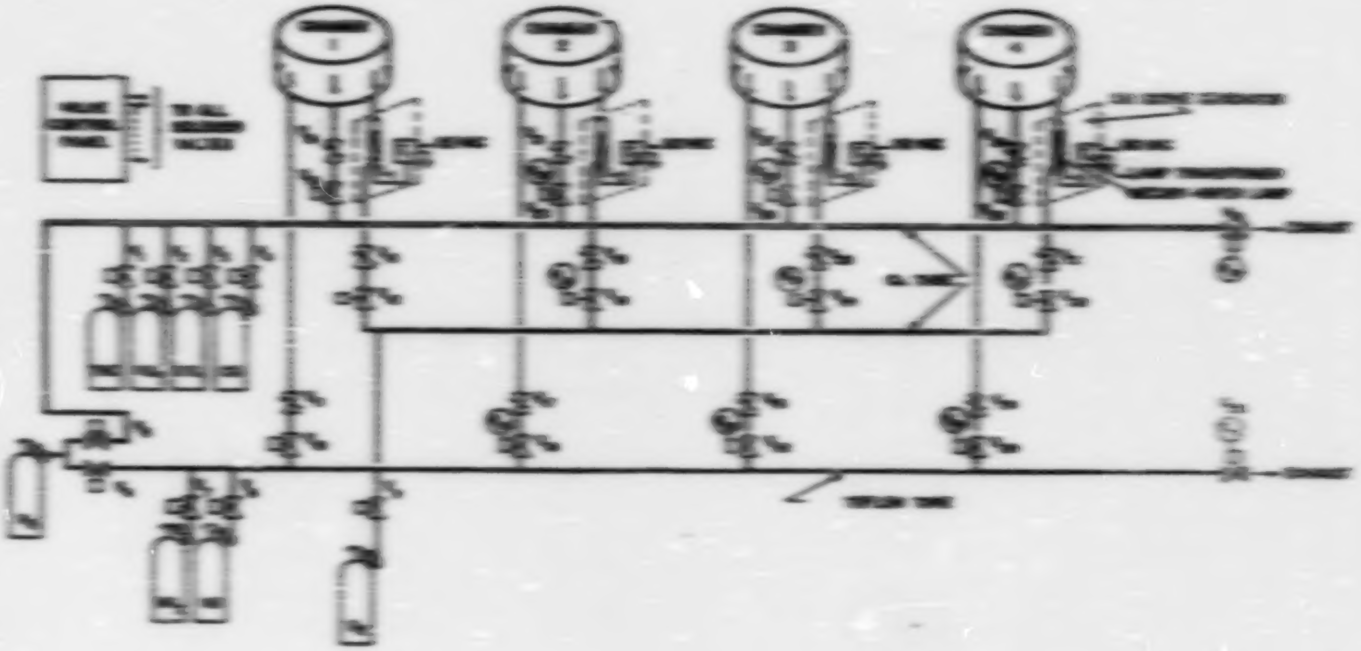

Figure 4. Reactant injection system, [illegible] smog chambers.

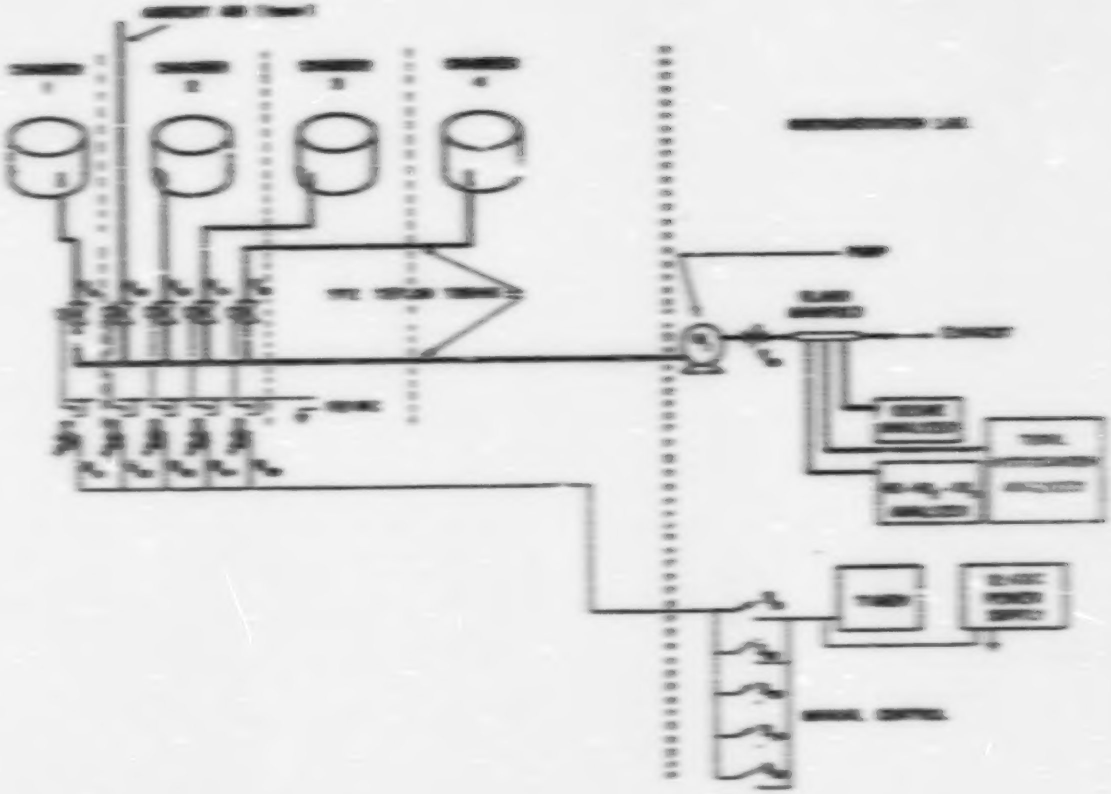
1
2
3
4
TIMER
MANUAL CONTROL
EXHAUST
TOTAL

Figure 5. Sampling system, [illegible] smog chambers.

CHARACTERIZATION

Sample Line

At all concentrations examined, there is a 20% loss of O_3 between the chamber and the O_3 instrument. All quoted O_3 concentrations have been corrected.

The Cleanup System

The air cleanup system routinely reduces the NO_x content of make-up air to a measured zero. The catalyst beds, as constructed, are capable of reducing nonmethane hydrocarbon (NMHC) to 0.01 ppmC. Electrical and thermal problems, however, sometimes result in a decrease of the NMHC concentration to only 0.50 ppmC. These problems are (at this writing) being eliminated.

Ozone Decay (8-1-75)

Dark phase (O_3 concentration ~0.85 ppm):

Chamber #1	$t_{1/2}$	~22 hours
Chamber #2	$t_{1/2}$	~27 hours
Chamber #3	$t_{1/2}$	~23 hours
Chamber #4	$t_{1/2}$	~30 hours

Light phase (O_3 concentration ~0.45 ppm):

Chamber #1	$t_{1/2}$	~10 hours
Chamber #2	$t_{1/2}$	~10 hours
Chamber #3	$t_{1/2}$	~11 hours
Chamber #4	$t_{1/2}$	~10 hours

Nitric Oxide Oxidation (7-11-75)

Sunrise to 1400 hrs (NO concentration ~0.55 ppm):

Chamber #1	.011 ppm hr^{-1}	~2.5 × thermal
Chamber #2	.005 ppm hr^{-1}	~1 × thermal
Chamber #3	.011 ppm hr^{-1}	~2 × thermal
Chamber #4	.009 ppm hr^{-1}	~2 × thermal

The THC reading during the above experiments were:

Chamber #1	0.05 ppmC
Chamber #2	0.13 ppmC
Chamber #3	0.02 ppmC
Chamber #4	0.07 ppmC

Clean Air Irradiation (7-10-75)

The air in the chambers was cleaned and irradiation was started at sunup (ca. 0530 EDT). The O_3 maxima occurred in the 1600-1700 sampling period.

Chamber #1	NMHC	NO_x	O_3 Max 1600-1700
Chamber #1	~0.10 ppmC	tr (<1 ppb)	0.15 ppm
Chamber #2	~0.04 ppmC	tr (~2 ppb)	0.14 ppm
Chamber #3	~0.16 ppmC	tr (<1 ppb)	0.15 ppm
Chamber #4	~0.24 ppmC	tr (<1 ppb)	0.16 ppm

Propylene-NO_x Irradiation (7-9-75)

Simultaneous propylene-NO_x runs were made with an approximate NMHC concentration of 1.20 ppmC and 0.35 ppm NO_x (10% NO_2).

Organics (ppmC)

Chamber	Background After Cleanup NMHC	Propylene	Total NMHC	NO_x ppm (10% NO_2)	O_3 Max ppm
Chamber #1	0.35	0.69	1.04	0.35	0.61 ppm
Chamber #2	0.45	0.82	1.27	0.36	0.70 ppm
Chamber #3	0.40	0.77	1.17	0.35	0.62 ppm
Chamber #4	0.42	0.93	1.35	0.38	0.71 ppm

Time NO_x Crossover	
Chamber #1	0933
Chamber #2	0927
Chamber #3	0924
Chamber #4	0857

Ozone maxima occurred between 1500 and 1540 (EDT).

SECTION V

DESIGN OF STUDY

RESEARCH PLAN

The original contract (EPA 68-02-1296) called for a series of experimental runs with 18 sets of conditions plus 6 replications. In subsequent talks with Dr. Basil Dimitriades, a program involving 37 sets of experimental conditions plus 7 replications (44 experimental runs) was discussed. Twenty of the 37 sets plus 4 replications were run for purposes of this contract (EPA 68-02-1296) and the remainder are being run as part of the subsequent contract (EPA 68-02-2207). Dilution rates are shown in Table 2. Before dilution was initiated, the chambers were operated in the batch mode. The dilution was initiated at the time designated in Table 3, and dilution continued for 24 hours. After 24 hours, dilution was terminated and the chambers were operated again in the batch mode.

The conditions for the extended project are put forth in Table 4. The conditions for the 20 sets of conditions accomplished for this contract are set forth in Table 1.

The concentrations ranges are:

NMHC (ppmC): 1-10

NO_x (20% NO_2) (ppm) : 0.1-1.0

The ratio range is:

NMHC/NO_x : 7-20

Figure 6 delineates all possible combinations with these concentrations and ratios.

Table 2. Dilution Rate (24-Hour Dilution)

Throughput in 24 Hours $\frac{F}{V} \times t$ in Percent V	Actual Flow Rate, $m^3 min^{-1} \times 10^2$	Percent Original Volume Left After 24 Hours of Dilution at the Specified Flow Rate	Percent Dilution in 24 Hours
300	5.83	5.0	95
150	2.92	22.3	77
50	0.96	60.7	39
0	Sample Replacement	96.0	4

Table 3. Selected Experimental Conditions, Contract (68-02-1296)

NMHC/NO_x Ratios: 99% Dilution in 24 Hours Starting at:	77% Dilution in 24 Hours Starting at:
Sunrise	NO_x Crossover
10/1	10/1
5/.71	5/.71
5/.24	5/.24
1/.1	1/.1
NO_x Crossover	NO_x Crossover
10/1	10/.75
5/.71	5/.50
5/.24	5/.36
1/.1	1/.14
1700	No Dilution (Batch)
10/1	10/1
5/.71	5/.71
5/.24	5/.24
1/.1	1/.1

Table 4. Experimental Conditions, Extended Project[a]

Time of Initiation of Dilution	% Dilution in 24 Hours	Reagent Concentrations HC/NO_x	Number of Runs
None (Batch)	0	10/1, 1/.1, 5/.71, 5/.24	4
Sunrise	30	10/1, 1/.1, 5/.71, 5/.24	4
	99	10/1, 1/.1, 5/.71, 5/.24	4
1700 EDT - RTP, N.C.	30	10/1, 1/.1, 5/.71, 5/.24	4
	99	10/1, 1/.1, 5/.71, 5/.24	4
NO_x Crossover	30	10/1, 1/.1, 5/.71, 5/.24	4
	77	10/1, 1/.1, 5/.71, 5/.24 10/.48, 10/.75, 5/.36, 5/.50, 1/.14	9
	99	10/1, 1/.1, 5/.71, 5/.24	4

Total Number, Sets of Conditions 37

Replications 7

Total Runs 44

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[a] See Table 3 for Runs on Contract (68-02-1296).

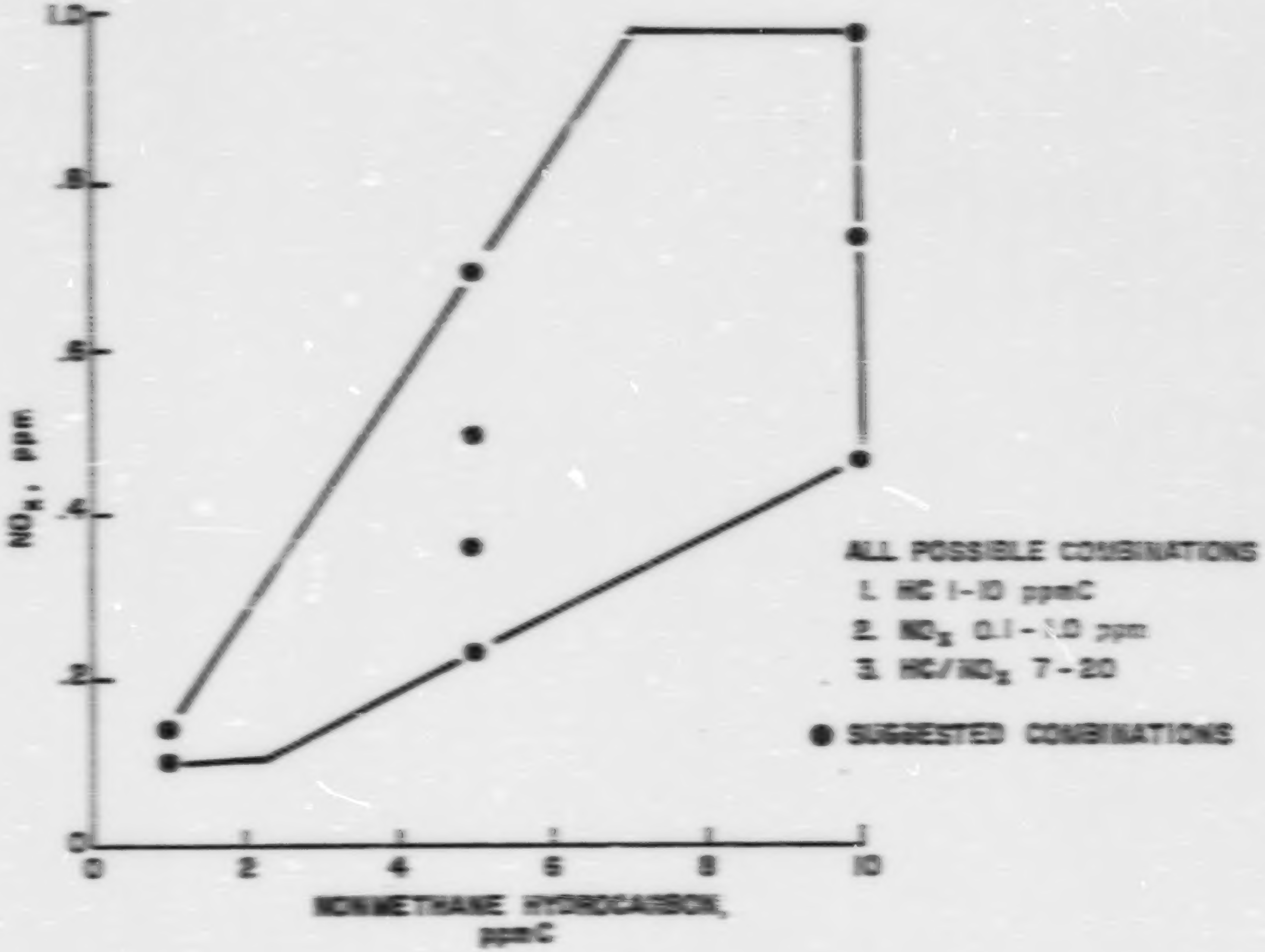

Figure 5. Range of all possible combinations of NO_x and nonmethane hydrocarbon concentrations used in experimental work.

The purpose of the study was to study the O_3-precursor relationship under conditions of simulated meteorological transport. Two facets of transport were employed, urban pollution mixtures were exposed to outdoor conditions for 60 hours beginning at sunrise the first day, and the urban pollution system was diluted with clean air. The dilution was initiated at different times of the day and continued at different rates for 24 hours, after which the system was run on a batch basis. Dilution was terminated after 24 hours because it is probable that in the eastern United States air with which the system is being mixed is just as polluted as the urban system it is diluting.

REAGENTS

The HC mixture used was constituted so as to represent a reasonable surrogate of Los Angeles air. The following fractions and ratios were determined on a carbon basis. The alkane/alkene/acetylene/aromatic percentages were 49/22/9/20. Propane, n-butane, isopentane and cylcopentane constituted the alkane fraction in ratios of 1.0/3.4/2.1/0.06. Propane represented itself; n-butane, the straight chain alkanes; isopentane, the branched chain alkanes; and cyclopentane, the cyclic paraffins. Ethylene, propylene, butene-1, trans-2-butene and 2-methyl-butene-2 constituted the alkene fraction in ratios of 1.0/0.32/0.39/0.21/0.29. Ethylene and propylene represented themselves, butene-1 represented terminally double-bonded compounds, butene-2 represented internally double-bonded compounds, and 2-methyl-butene-2 represented branched-chain olefins. The aromatic compounds were represented by toluene. In all cases, the NO_x injected was 20% NO_2 and 80% NO.

MEASUREMENT METHODS

Continual Instrumental Measurements

Ozone, NO, NO_2, total hydrocarbons (THC), methane (CH_4), and CO were measured on a continual basis by use of automated instruments described below. Calibration was performed prior to each three-day experiment.

Ozone was detected by use of the chemiluminescent reaction between O_3 and ethylene. The Bendix instrument was used. A stable ultraviolet light O_3 generator of known output serves as the calibration source. The output of the O_3 generator itself was determined by the neutral-buffered KI procedure for O_3 and/or by gas-phase titration of a certified standard of NO in nitrogen mixture.

Nitric oxide and NO_2 were both detected by use of the chemiluminescent reaction between NO and O_3. In this instrument the NO_2 is catalytically converted to NO. A Bendix instrument and a TECO Model 14 were employed. Calibration of the NO and NO_x channels of the instrument was performed by dilution of a certified cylinder of NO in N_2. The NO_2 channel was calibrated with NO_2 produced from the gas-phase titration of known NO concentrations with O_3 from the calibrated ozone generator.

Total hydrocarbons, CH_4, and CO were determined by an automatic environmental chromatograph equipped with a flame ionization detector. The Beckman Model 6800 was employed. Calibration was performed by introduction of a certified mixture of CH_4 and CO. This instrument was calibrated at 12-hour intervals during each three-day experiment.

Periodic Measurements: Hydrocarbons, Oxidant, Nitrogen Dioxide, Formaldehyde, and Condensation Nuclei

Individual hydrocarbons and selected products of photochemical reaction were determined by gas chromatographic separation and flame ionization detection from samples taken twice daily. A modified Perkin-Elmer Model 900 chromatograph was used.

Air samples taken from ports at the individual reaction chambers were passed through a metal bellows pump into a Tedlar bag. A permanganate in-line scrubber destroyed the O_3 and thus stabilized the HC composition of the sample.

A specific volume of sample from the Tedlar bag was trapped in a 0.0032-m ID stainless steel loop which had been immersed in liquid oxygen. The trap was connected to the chromatograph, heated, and its contents passed into the column.

Low-molecular-weight hydrocarbons (C_2-C_5) were separated by a 1.8-m × 0.0032-m SS column packed with n-octane on Porasil. The column was at 23°C with a carrier flow rate of 12 ml per minute.

High-molecular-weight hydrocarbons (including aromatics) were separated by a 1.8-m × 0.0032-m SS column packed with GP 5% SP-1200/5% Bentone 34 on 100/120 Supelcoport. The column was at 75°C with a carrier flow rate of 20 ml per minute.

The chromatograph detector response and retention times were reestablished on at least every second working day by introduction of known hydrocarbons from certified cylinders of ±1% accuracy. A Hewlett-Packard Model HP-3352 gas chromatographic data system acquired peak area data and printed out the results on a teletype.

Ozone, NO_2, and formaldehyde (CH_2O) were determined by wet chemistry techniques employing impingers and spectrophotometric detection. The neutral-buffered potassium iodide procedure was used for O_3 determination, and the Saltzman procedure was used for NO_2 determination (ref. 2). Formalydehyde was collected and detected using the chromotropic acid procedure, Intersociety Committee, Procedure No. 110 (ref. 3). Calibration curves and blanks were prepared periodically according to the procedures referenced above. The determinations were performed twice daily, at 0900 and 1600 EDT.

A measure of condensation nuclei (CN) was determined four times per day. A Gardner Associates Type CN detector was used. The sample was taken directly from the chamber through a 1-m length of Teflon tubing. The manufacturer's calibration was used.

Radiation

Total solar radiation (TSR) was followed with a Kipp and Zonen solarimeter. This instrument was used as a guide to the radiation behavior for the day's experiment. The TSR and UV radiometer data collected by the EPA Division of Meteorology at a point approximately 500 m distant from the RTI smog chamber site were used for quantitative purposes.

SECTION VI

DISCUSSION OF RESULTS

The results of this study can be used to explain many of the major features of the high nonurban O_3 concentrations observed in the eastern United States in recent years. This air is generally characterized by concentrations of several tens of parts per million of NMHC (e.g., 0.30 ppm), a few tens of parts per billion (e.g., 0.015 ppm) of NO_x and generally 0.08 to 0.20 ppm of O_3. (Data from gas chromatographic analyses of individual hydrocarbons are presented in Appendix A. Ozone, NO_x, NMHC, CO, and solar radiation data are presented as computer-printed graphs in Appendix B. Because the individual data are too voluminous for inclusion in this report, they have been supplied separately to EPA on computer cards and as computer-generated listings.)

It is postulated that the chemistry of the generation of high O_3 concentrations downwind from a city involves the following three major processes:

1. Once generated in a "spent photochemical" system (i.e., low NO_x, virtually no alkenes) and, out of touch with new sources of precursors, O_3 is not destroyed rapidly and can persist overnight in high concentrations.

   The half-life of O_3 in the field, held aloft, away from pollution sources was estimated from one set of vertical O_3 soundings to be 20 to 30 hours. This is not unreasonable for O_3 in a mature photochemical system out of touch with O_3-destructive agents which may be present in recently polluted air parcels. The half-lives of O_3 in the chamber runs generally were between 3 and 10 hours.

2. For systems of comparable hydrocarbon/NO_x ratio, dilution of the system, whether reduction of the initial concentrations or dynamic dilution after the initiation of irradiation, leads to the generation of more O_3 per precursor molecule.

3. The third process included in the generation of nonurban O_3 in high concentrations involves the NO-NO_2-O_3 cycle. As a photochemical system reacts, the olefins disappear more rapidly than the aromatics and the alkanes. The NO_x concentration is reduced even more rapidly

than the NMHC. It is postulated that as the NMHC/NO_x ratio increases, the hydroxyl radicals generated in the system react in larger and larger proportions with the hydrocarbons than with NO_2. Reactions of an hydroxyl with an organic molecule leads eventually to the oxidation of NO to NO_2, thus preserving one O_3 molecule. Reaction of the hydroxyl with NO_2 leads to the formation of $HONO_2$. This reaction removes an NO_x molecule from the system and does *not* lead to the generation of an O_3 molecule. When the NO_x molecules are diluted sufficiently, the absolute rate of generation of O_3 is so low that it cannot replace O_3 lost by various extraneous reactions always taking place in the system. In reaction and dilution, depending on original conditions, the net O_3 generated per NO_x cycle increases more rapidly than the total decrease in O_3 by dilution, destruction, and synthesis inhibition--up to a point. At some level the NO_x molecules become so few that they cannot supply a net increase in O_3 in the face of the various destructive processes such as photochemically related destruction of O_3, heterogeneous destruction, and reaction with substances generally not considered as part of the photochemical oxidant systems.

Data from this study support the hypothesis that these processes are active in the generation of high rural O_3 concentrations.

OZONE-PRECURSOR RELATIONSHIPS

The data were examined to determine the effect of concentration and ratio of the measured oxidant precursors at the beginning of solar irradiation on subsequent O_3 maxima and on net O_3 generated. The pertinent data are summarized in Tables 5, 6, 7, 8, 9, and 10.

The relationship among initial concentrations of NO_x and NMHC concentration and subsequent O_3 maximum concentration on second and third days of irradiation as revealed in this study is, as expected, quite different from that of the more classical smog chamber studies (ref. 1). Tables 11, 12, 13, and 14 illustrate this point. The ranges of concentrations and NMHC/NO_x ratios used in making the tables were chosen arbitrarily in an attempt to place a number of cases in each category. These data are plotted in Figures 7, 8, and 9.

Hydrocarbon mixtures on the second and third day of irradiation were, as expected, much lower in olefins than was the initial mixture. On the second and third day of solar irradiation the butene was seldom as high as 2 ppbC, propylene was at or (usually) below 2 ppbC (except in the batch runs when it was 2, 5, 12, and 15 ppbC on the second day) and ethylene was generally in the low 10's of ppbC. The mix contained essentially alkanes and aromatics by the second day. (Hydrocarbon analyses are presented in Appendix A.)

The greater the NO_x concentration at sunrise on the second and third days the greater the subsequent net O_3 (ΔO_3) generated; for example, the 1-5 ppb NO_x concentrations produced an average ΔO_3 of 0.149 ppb; 6-8 ppb NO_x, a ΔO_3 of 0.171 ppm; 9-14 ppb NO_x, 0.180 ppm ΔO_3; and 15-53 ppb NO_x, 0.241 ΔO_3. For the same ranges of NO_x the subsequent maximum O_3 concentrations were 0.180 ppm, 0.254 ppm, 0.259 ppm, and 0.454 ppm. This also shows that average daily minimum increased with increasing NO_x range: 0.031, 0.083, 0.079, and 0.213 ppm (see Figure 7).

Average ΔO_3 values corresponding to NMHC concentration ranges for: 0-0.49 ppmC was 0.157 ppm; 0.50-0.99 was 0.180; 1.00 to 1.99, was 0.183; and ≥2.00, was 0.257. The corresponding maximum O_3 concentrations were 0.175, 0.241, 0.301, and 0.623 ppm.

Table 5. Selected Results From the July 17-19 Two-Day Chamber Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NOx Concentrations ppmC/ppm	NMHC/NOx Ratio	Maximum O_3 First Day ppm	Subsequent Days	Concentrations (ppm) at Sunrise		NMHC/NOx Ratio	Min O_3 ppm	Max O_3 ppm	Max O_3 ppm	% Solar Rad. at O_3 Max (Langley's)
						NO_x	NMHC					
Chamber No. 1 July 17-18	50 8 Sunrise NONE Start	1.68 0.425	24.2	0.322	2	0.024	0.478	22.6	.020	.200	.255	427.6"
					3							
Chamber No. 2 July 17-18	NONE	3.71 0.125	29.7	0.385	2	0.023	0.330	22.8	.080	.282		427.6
					3							
Chamber No. 3 July 17-18	NONE	3.48 0.280	12.9	0.242	2	0.023	0.365	24.8	.002	.255	.234	422.6
					3							
Chamber No. 4 July 17-18	NONE	3.33 0.596	23.6	0.232	2	0.022	0.320	25.4	.002	.226	.119	426.8
					3							

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Table 6. Selected Results from the July 22-24 Three-Day Chamber Runs

Date Chamber No.	Percent Dilution Time of Dilution Initiation	Initial NMHC/NOx Concentrations ppmC/ppm	NMHC/NOx Ratio	Maximum O_3 First Day ppm	Subsequent Days	Concentration (ppm) at Sunrise NOx	Concentration (ppm) at Sunrise NMHC	NMHC/NOx Ratio*	Min O_3 ppm	Max O_3 ppm	Max O_3 ppm	Solar Rad. at O_3 Max (Langley's)
Chamber No. 1 July 22-24	[illegible] 1700	11.45/.530	22.1	1.57	2	0.025	1.78	119.7	.002	.185	.132	427.8
					3	0.010	1.07	107.3	.026	.323	.187	481.6
Chamber No. 2 July 22-24	1700	6.67/.331	23.4	0.950	2	0.029	1.30	144.4	.025	.236	.122	481.1
					3	0.007	0.94	134.3	.020	.262	.272	482.6
Chamber No. 3 July 22-24	1700	4.11/.600	6.9	1.196	2	0.010	1.18	118.0	.005	.220	.094	487.8
					3	0.707	0.89	127.1	.021	.268	.257	481.4
Chamber No. 4 July 22-24	1707	3.76/.183	27.1	0.625	2	0.026	0.85	157.5	.023	.086	.074	487.8
					3	0.015	0.72	144.2	.020	.225	.217	481.4

Table 7. Selected Results from the July 28-30 Three-Day Chamber Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO$_x$ Concentrations ppmC/ppm	NMHC/NO$_x$ Ratios	Maximum O$_3$ First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO$_x$ Ratios	Min O$_3$ ppm	Max O$_3$ ppm	Max O$_3$ ppm	Σ Solar Rad. at O$_3$ Max (Langley's)
						NO$_x$	NMHC					
Chamber No. 1	95% @ 0830	7.02/.967	7.3	1.062	2	0.007	0.84	120.0	.023	.286	.263	515.4
July 28-30					3	0.009	0.85	94.4	.050	.240	.190	421.2
Chamber No. 2	0840	4.26/.225	18.9	0.604	2	0.003	0.77	256.7	.006	.212	.206	535.2
July 28-30					3	0.005	0.76	152.0	.036	.190	.152	420.6
Chamber No. 3	0840	3.95/.715	5.5	0.667	2	0.005	0.42	84.0	.013	.214	.201	534.6
July 28-30					3	0.005	0.55	110.0	.037	.190	.153	397.8
Chamber No. 4	0850	1.15/.105	11.0	0.325	2	0.002	0.55	275.0	.003	.175	.172	541.2
July 28-30					3	0.003	0.63	210.0	.042	.167	.125	427.2

Table 8. Selected Results from the August 4-6 Three-Day Runs

Run Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO$_x$ Concentrations ppmC/ppm	NMHC/NO$_x$ Ratio	Maximum O$_3$ First Day ppm	Day of Irradiation	Precursors (ppm) at Sunrise		NMHC/NO$_x$ Ratio at Sunrise^a	Min O$_3$ ppm	Max O$_3$ ppm	Net O$_3$ ppm	Σ Solar Rad. at O$_3$ Max (Langley's)
						NO$_x$	NMHC					
Chamber No. 1 August 4-6	7% @ 0810	$\frac{7.15}{.980}$	7.3	1.239	2	0.027	1.23	45.6	.116	.479	.365	354.7
					3	0.022	0.79	35.9	.174	.285	.139	316.4
Chamber No. 2 August 4-6	0830	$\frac{4.62}{0.232}$	19.9	0.806	2	0.009	0.88	97.8	.056	.366	.322	511.2
					3	0.006	0.62	103.3	.126	.233	.105	328.4
Chamber No. 3 August 4-6	0800	$\frac{4.42}{.675}$	6.5	0.556	2	0.010	0.74	74.0	.096	.350	.256	511.2
					3	0.007	0.58	82.9	.114	.238	.124	281.7
Chamber No. 4 August 4-6	0805	$\frac{3.38}{.337}$	10.2	0.482	2	0.001	0.61	610.0	.042	.216	.173	354.7
					3	0.004	0.47	117.5	.056	.179	.123	328.4

Table 9. Selected Results From the August 9-10 Three-Day Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO$_x$ Concentrations ppmC/ppm	NMHC/NO$_x$ Ratios	Maximum O$_3$ First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO$_x$ Ratios	Min O$_3$ ppm	Max O$_3$ ppm	Sec O$_3$ ppm	Σ Solar Rad. at O$_3$ Max (Langley's)
						NO$_x$	NMHC					
Chamber No. 1 August 9-10	77% @ 0940	$\frac{5.81}{0.717}$	8.1	0.981	2	0.020	1.17	58.5	.230	.400	.300	513.0
					3	0.014	0.52	37.1	.136	.320	.182	309.6
Chamber No. 2 August 9-10	0850	$\frac{3.52}{0.347}$	10.2	0.841	2	0.010	0.64	64.0	.063	.297	.230	570.0
					3	0.008	0.62	78.0	.105	.231	.122	309.6
Chamber No. 3 August 9-10	0940	$\frac{3.09}{0.481}$	6.4	0.688	2	0.012	0.62	51.7	.074	.280	.214	564.0
					3	0.010	0.84	84.0	.100	.248	.148	266.4
Chamber No. 4 August 9-10	0940	$\frac{0.93}{0.144}$	6.5	0.378	2	0.002	0.43	215.0	.050	.179	.129	570.0
					3	0.004	0.71	178.0	.071	.163	.092	306.0

Table 10. Selected Results from the August 13-16 Three-Day Runs

Date Chamber No.	Dynamic Dilution, Time of Dilution Initiation	Initial NMHC/NOx Concentrations ppmC/ppm	NMHC/NOx Ratios	Maximum O3 First Day ppm	Subsequent Days	Concentrations (ppm) at Sunrise		NMHC/NOx Ratios	[illegible] O3 ppm	[illegible] O3 ppm	[illegible] O3 ppm	Σ Solar Rad. at O3 Max (Langleys/d)
						NOx	NMHC					
Chamber No. 1 August 13-16	Static	7.23/0.958	8.2	1.37	2	0.053	3.78	71.3	.507	.730	.257	585.2
					3	0.035	3.81	91.2	.270	.624	.344	567.8
Chamber No. 2 August 13-16		4.36/0.225	19.5	0.886	2	0.122	2.62	215.1	.388	.525	.139	585.2
					3	0.018	2.10	116.7	.228	.480	.228	568.4
Chamber No. 3 August 13-16		3.81/0.676	5.6	0.987	2	0.039	2.48	63.6	.425	.698	.294	888.6
					3	0.029	1.93	151.6	.246	.474	.278	578.4
Chamber No. 4 August 13-16		1.36/0.203	15.2	0.547	2	0.011	1.30	118.2	.333	.336	.122	581.6
					3	0.007	1.13	161.4	.231	.259	.268	594.6

Table 11. Net Ozone Generated on Second and Third Days of Irradiation as a Function of Oxides of Nitrogen and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio

[illegible]	NO_x Range ppb 1 - 5		6 - 8		9 - 14		15 - 22	
3-49					[illegible] [illegible] *[illegible]	[illegible] avg.	[illegible] [illegible]	[illegible] avg.
[illegible]								
50-99	[illegible]	[illegible] avg.	*[illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] [illegible] [illegible] *[illegible] *[illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] [illegible] [illegible] *[illegible]	[illegible] avg.
[illegible]								
100-199	*[illegible] *[illegible] *[illegible] *[illegible] *[illegible]	[illegible] avg.	[illegible] *[illegible] *[illegible] *[illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] [illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] *[illegible] *[illegible]	[illegible] avg.
[illegible]								
[illegible]	[illegible] [illegible] [illegible] [illegible] [illegible] *[illegible]	[illegible] avg.						
Avg. [illegible]	Avg. [illegible]		Avg. [illegible]		Avg. [illegible]		Avg. [illegible]	

*Indicates 3rd-Day Values.

Table 12. Maximum Ozone Concentration on Second and Third Days of Irradiation as a Function of Oxides of Nitrogen and Nonmethane Hydrocarbon/ Oxides of Nitrogen Ratio

[illegible]	NO_x Range ppb 1 – 5		6 – 8		9 – 14		15 – 50	
[illegible]					[illegible] [illegible] *[illegible]	[illegible] avg.	[illegible] [illegible]	[illegible] avg.
[illegible]								
[illegible]	.274	.274 avg.	*[illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] [illegible] [illegible] *[illegible] *[illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] [illegible] [illegible] *[illegible]	[illegible] avg.
[illegible]								
[illegible]	*[illegible] *[illegible] *[illegible] *[illegible] *[illegible]	[illegible] avg.	[illegible] *[illegible] *[illegible] *[illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] [illegible] *[illegible]	[illegible] avg.	[illegible] [illegible] *[illegible] *[illegible]	[illegible] avg.
[illegible]								
[illegible]	[illegible] [illegible] [illegible] [illegible] [illegible] *[illegible]	[illegible] avg.						
Avg. [illegible]		Avg. [illegible]		Avg. [illegible]		Avg. [illegible]		Avg. [illegible]

*Indicates 3rd-Day values.

Table 13. Net Ozone Generated on Second and Third Days of Irradiation as a Function of Nonmethane Hydrocarbon and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio

NMHC/NOx Ratio ppm	NMHC Range ppmC 0 - .49		.50 - .99		1.00 - 1.99		≥2.00	
0-49	.186 .161 .158 .115	.161 avg.	*.182	.182 avg.				
.165								
50-99	.207	.207 avg.	.312 .266 .238 .274 *.198 *.119 *.128	*.137 *.177 .206 avg.	.365 .300	.333 avg.	.247 .371 *.244	.274 avg.
.235								
100-199	*.123	.123 avg.	.262 *.238 *.257 *.207 *.192 *.153 *.105	*.258 .181 avg.	.370 .323 .394 .323 *.305 *.335 *.290	.340 avg.	.135 *.238	.187 avg.
.163								
>200	.129	.129 avg.	.276 .206 .172 .173 *.125	.190 avg.				
Avg. .147		Avg. .157		Avg. .188		Avg. .303		Avg. .237

*Indicates 3rd-Day Values.

Table 24. Maximum Ozone Concentration on Second and Third Days of Irradiation as a Function of Nonmethane Hydrocarbon and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio

NMHC/NOx Ratio ppm \ NMHC Range ppmC	0 - .49	.50 - .99	1.00 - 1.99	≥2.00
0-49	.220 .191 .155 .116 [illegible] avg.	*.318 .318 avg.		
.194				
50-99	.274 .274 avg.	.365 .350 .293 .288 *.240 *.253 *.238 *.231 *.273 [illegible] avg.	.479 .483 .481 avg.	.724 .716 *.634 [illegible] avg.
.304				
100-199	*.179 .179 avg.	.286 *.202 *.[illegible] *.[illegible] *.[illegible] *.[illegible] *.[illegible] *.163 [illegible] avg.	.285 .138 .119 .188 *.322 *.474 *.259 [illegible] avg.	.335 *.423 [illegible] avg.
.[illegible]				
>200	.179 .179 avg.	.285 .272 .175 .214 *.167 [illegible] avg.		
Avg. .[illegible]	Avg. .225	Avg. .241	Avg. .301	Avg. .[illegible]

*Indicates 3rd-Day Values.

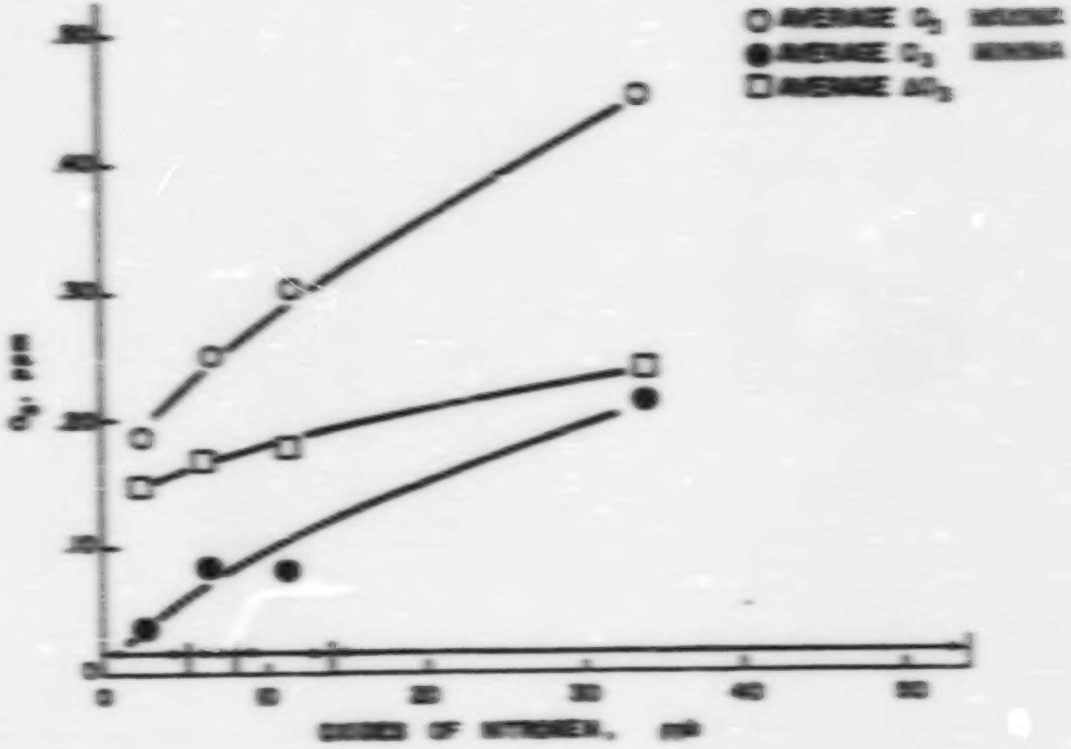

Figure 7. Average maxima, minima, and ΔO_3 concentrations as a function of NO_x concentrations at sunrise on the second and third days of irradiation.

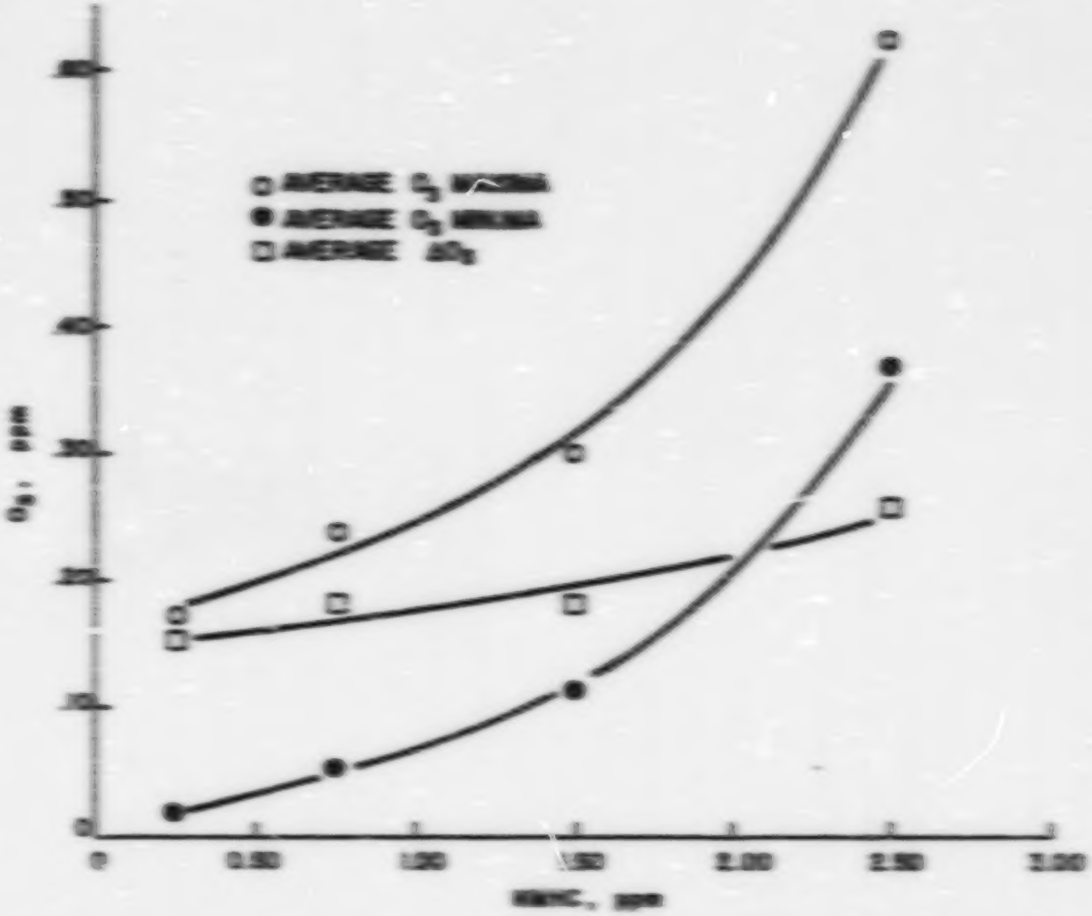

Figure 8. Average maxima, minima, and ΔO_3 concentrations as a function of nonmethane hydrocarbon concentrations on the second and third days of irradiation.

Increasing hydrocarbon concentration at sunrise of the second and third days tended also to increase the subsequent net O_3 generation as can be seen in Figure 8.

For the NMHC/NO_x ratios, the ΔO_3 for the range 0-49 was 0.163; for 50-99 it was 0.235; for 100 to 199 it was 0.161; and for $\geq$200 it was 0.147. Maximization of O_3 concentration occurred in the 50-99 range (see Figure 9).

It can be demonstrated, in any case, that low concentrations of NO_x (i.e., 0-5 ppb, within the noise level of the chemiluminescent NO_x meters) will generate O_3 in concentrations above the NAAQS. In almost all cases (the exceptions will be mentioned below) the second-day net O_3 generated was greater than the third-day net O_3.

Although no PAN data have been obtained, the difference between NO_2 determined by the Saltzman procedure and the chemiluminescent instrument indicates the presence of nitroxy compounds other than NO and NO_2.

In general, second-day maximum net O_3 generation was greater than third-day net O_3, which was expected (Tables 6 and 10). In the static (no dilution) runs and in the runs diluted 95% in 24 hours (dilution initiated at 1700 of the first day), the reverse was the case, even though the cumulative sunlight to time of O_3 maximum was comparable for the series of 2 days.

Although there is no readily apparent explanation of this anomaly in the data, it should be noted that at the time of maxima in the dilution runs on the second day, the system was still operating in the dilution mode. On the third day it was operating in the batch mode. On the second day, the combination of destruction plus mechanical removal of O_3 must be balanced against synthesis whereas on the third day only chemical reaction was removing O_3 as it was generated.

In the case of the static or batch runs, the explanation for a greater net O_3 generation on the third day than the second has to be different, but again there is not an immediately apparent reason for the difference.

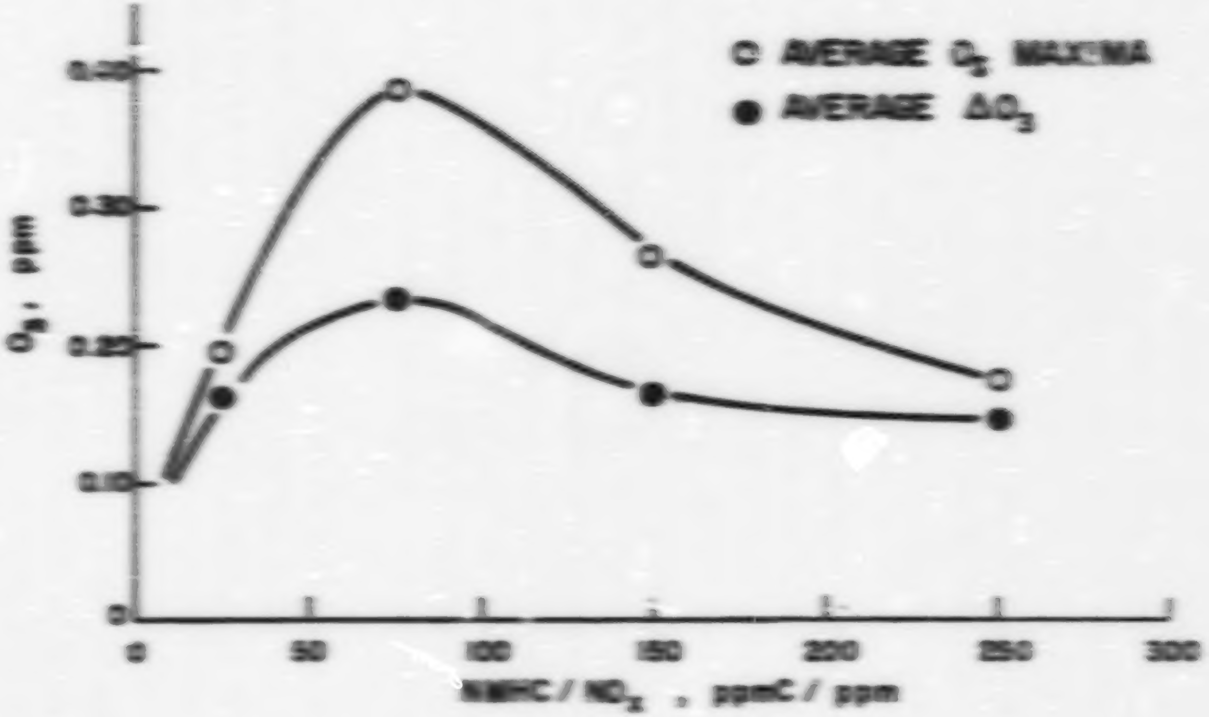

Figure 9. Average maxima and ΔO_3 as a function of nonmethane hydrocarbon to oxides of nitrogen ratio.

"FOSSIL" OZONE

One of the processes which are operative in the occurrence of high concentrations of O_3 in rural areas is the low rate of O_3 destruction in photochemically "spent" pollution systems. ("Spent" means here that the system has been reacting photochemically, the NO_x concentrations are low (a few parts per billion), and the olefinic content of the air has been exhausted, or nearly so.) This O_3 is often referred to as "fossil" ozone, perhaps an unfortunate adjective to apply, but the lifetime of "fossil" O_3 is seldom, if ever, specified, even vaguely.

Ozone measured at or near the ground (e.g., at 1.0 m) has the opportunity to engage not only in gas-phase homogeneous reactions including photolysis, but also in heterogeneous reactions with the ground and other surfaces.

Under conditions of atmospheric subsidence, there is the possibility of considerable thermal layering of the air with a considerable reduction of mass transport across thermal boundaries. At night, for example, a radiation inversion can be [illegible]d in the lower part of the previous day's mixing layer. The air between the bottom of the subsidence inversion and the top of the radiation inversion is effectively cut off from pollution emissions at the ground and dilution from above. Ozone, trapped in the remnant of the mixing layer, has only "left-over" precursors to react with, so an estimation of its duration will indicate how important both the trapped ozone and the subsequent synthesis are in maintaining the observed nonurban levels of O_3 concentrations.

Nighttime half-lives for ground level O_3 calculated from the hourly average from three of the field stations in the 1974 RTI field study were 8.0, 8.2, and 9.7 hours (assuming first order decay). Calculated roughly from the ground level O_3 values at Wilmington, Ohio (Figure 10), the half-life was about 10 hours. Calculated for the 600-m level in the same figure, the half-life of O_3 aloft, out of touch with ground-based sources of pollution, was roughly 20 hours. (These last 2 calculations were based on the assumption that the vertical profile of O_3 concentrations would be the same at 0700 on August 2 as on August 1.) The O_3 destruction aloft, above the radiation inversion layer, is likely to be more representative of "fossil"

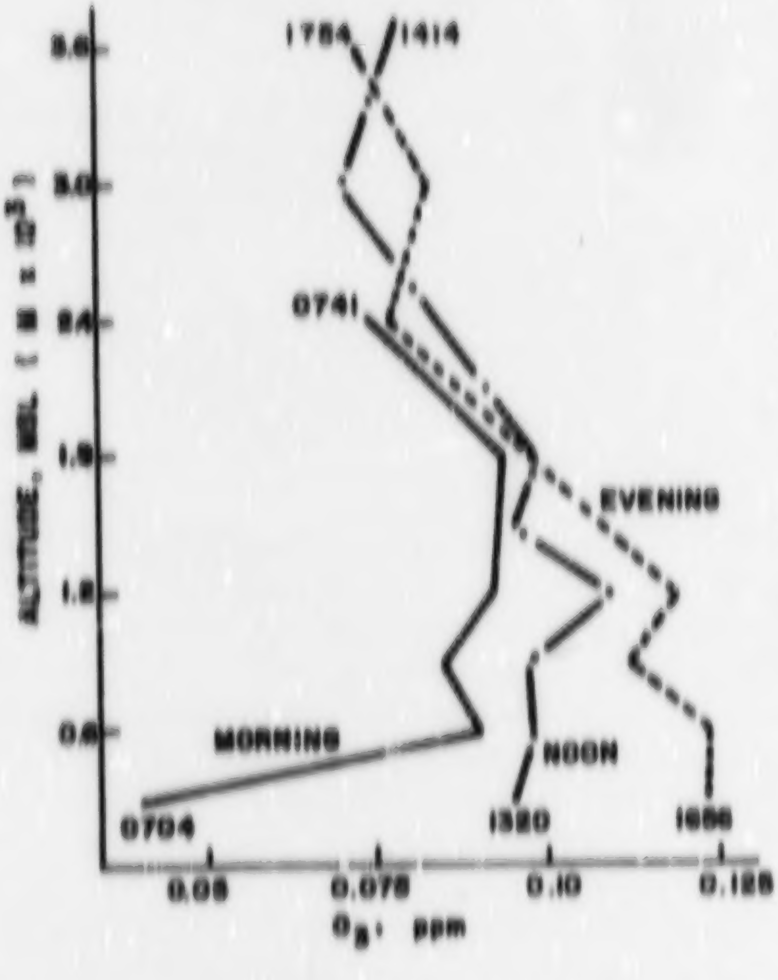

Figure 10. Vertical ozone soundings, August 1, 1974, Wilmington, Ohio.

O_3 conditions than O_3 destruction near the earth.

Dark-phase half-lives ($t_{1/2}$) for O_3 in these chamber runs were calculated and are presented in Table 15. These half-lives were calculated from nighttime O_3 data taken at 0200 and 0500 when no dilution was occurring.

To get a feel for the dark gas-phase destruction of O_3, consider the following table. Calculating O_3 destruction as a first order function with an assumed constant concentration of NO_2, the concentration of NO_2 was calculated which would be required by the listed half-lives.

HALF-LIVES, Hours	CONSTANT CONCENTRATION OF NO_2 NECESSARY, ppm
1	.231
5	.046
10	.023
20	.012
30	.008
40	.006
50	.005

Calculations using most olefins would yield similar concentrations. Nitrogen dioxide can account for much of the O_3 disappearance at night in the chambers, but intermediates, such as aldehydes, may also contribute to dark phase O_3 decay both in chambers and in rural air.

In any event, a few hours half-life is sufficient to account for persistence of O_3 at detectable concentrations overnight. On the other hand, a half-life of 10 hours (it would be shortened in the sunlight) would reduce 0.200 ppm O_3 to .001 in 77 hours (3 days). This should offer an initial estimate of how far (or how long) "fossil" O_3 can be important without ongoing O_3 synthesis. Obviously the duration of significant concentrations of "fossil" O_3 depends on many factors, including the original urban concentration of O_3. It is hardly likely that "fossil" O_3 alone, without concurrent daytime synthesis, can deliver O_3 concentrations in excess of the oxidant NAAQS to nonurban sites where transport processes have taken as long as 3 days. Therefore, persistence of O_3 in a "spent" photochemical

Table 15. Dark Phase Ozone Half-Lives in Smog Chamber Runs

Date	Experimental Type	Chamber Number	Max $[O_3]$ Previous Day ppm	$[O_3]$ at 2200 ppm	Half-Life ($t_{1/2}$) hrs
July 24	Dilution 95% * Initiated at 1700	1	0.185	0.066	4.3
		2	0.138	0.048	3.6
		3	0.119	0.038	11.6
		4	0.089	0.025	13.3
July 30	Dilution 95% Initiated at NO_x Crossover	1	0.256	0.102	6.4
		2	0.212	0.085	6.2
		3	0.214	0.076	7.4
		4	0.175	0.083	7.8
August 6	Dilution 77% Initiated at NO_x Crossover	1	0.479	0.311	14.9
		2	0.366	0.243	11.6
		3	0.350	0.213	10.0
		4	0.214	0.109	7.1
August 10	Dilution 77% Initiated at NO_x Crossover	1	0.400	0.218	16.6
		2	0.293	0.175	14.2
		3	0.298	0.170	19.2
		4	0.179	0.109	14.2
August 13	Batch	1	1.378	0.776	33.5
		2	0.886	0.561	42.9
		3	0.897	0.567	50.3
		4	0.549	0.415	265.4
August 14	Batch	1	0.724	0.422	19.9
		2	0.525	0.323	27.2
		3	0.786	0.352	54.5
		4	0.336	0.252	449.6

*Mechanical dilution had been terminated prior to the time periods chosen for half-life calculations.

system appears to be important in the appearance of high nonurban concentrations of O_3, but usually must be supplemented by additional synthesis. To calculate half-life:

$$\ln \frac{C_0}{C} = k_t\, t = (k_s + k_p)\, t$$

C_0 = O_3 concentration at 0200

C = O_3 concentration at 0500

t = 0500 - 0200 = 3 hours

k_t = total rate = $k_s + k_p$

k_s = dark-phase rate constant from measured O_3 decay in clean chamber air (system blank)

k_p = rate constant in aged photochemical system

Solve for k_t; and subtract k_s from k_t to obtain k_p.

$$t_{1/2} = \frac{\ln 2}{k_p}$$

DILUTION EFFECT

Decrease of concentrations of precursors (at the same NMHC/NO_x ratios) both by dynamic dilution and by decreasing initial concentrations in static systems resulted in an increase in the efficiency of O_3 generation per unit amount of precursors. In no case, when the initial precursors were at the same NMHC/NO_x ratio and were diluted, was the resultant net O_3 concentration decreased by a similar percentage. In the batch runs, the decrease of O_3 concentrations was 59% for a 95% reduction of the initial concentration (10/1.0 to 1.0/0.1, hydrocarbon to NO_x).

The effect of dynamic dilution is shown in Figure 11, which shows the second-day O_3 concentrations for 3 dilutions. The highest O_3 was obtained by the batch system (0.72 ppm) with 100% of the original system left, the second highest O_3 was obtained in a 77% dilution system (0.40 ppm), and the lowest O_3 at 95% dilution (0.29 ppm). Dilution was initiated at the time of NO_x crossover in both dilution systems. With 23% of the original system left, 75% as much O_3 was found as compared to the undiluted system and with 5% of the original system left, 40% as much O_3 was found.

If one compares the net O_3 increase (ΔO_3) (above minimum) for the second day, the chamber with 100% of the original system left had a ΔO_3 of 0.20 ppm while the system with 5% of the original system left had a ΔO_3 of 0.26 ppm. Total solar radiation was greater in the case of the static run. The net generation of O_3 was greater in the diluted case.

The time of initiation of dilution appears to influence second- and third-day ozone generation, but the data were too few to allow full delineation of the processes at work. The most notable effect of the time of initiation appears in the runs in which dilution was initiated at 1700. In these runs the net O_3 generated on the third day was approximately 2 to 3 times (1.9 to 2.9) as great as on the second day. The explanation may be that on the second day, mechanical dilution was decreasing the O_3 concentration at a rate which suppressed accumulation, enough to account for the low net generation, relative to the third day.

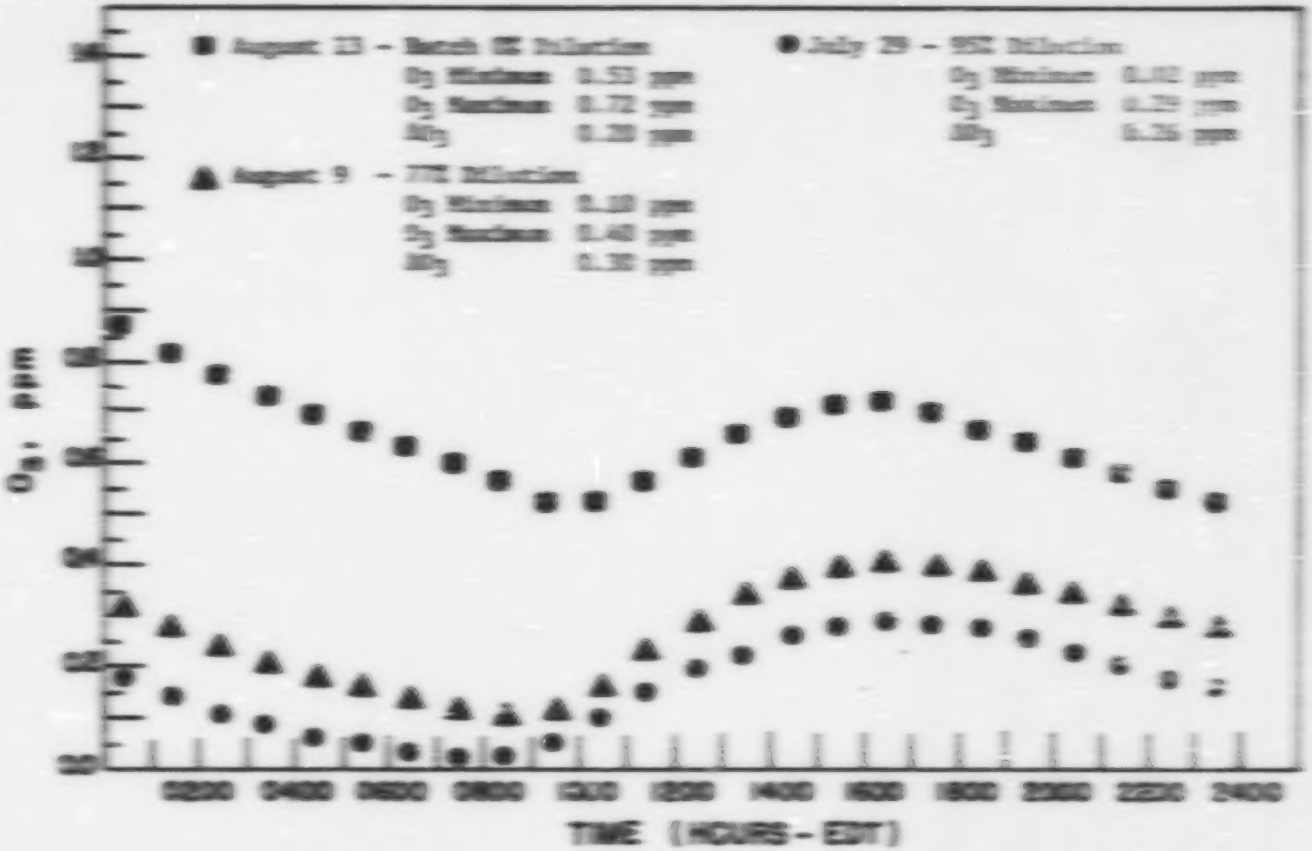

Figure 11. Ozone profiles over second-day irradiations for same initial conditions and different dilutions in Chamber #1.

These data indicate that dilution of an O_3-producing photochemical system does not reduce the maximum or the net O_3 concentration in direct proportion to the extent of dilution. This increased efficiency of O_3 production under dilution conditions is also supported by other findings (ref. 4). The dilution effect, therefore, is expected to be a significant contributor to the occurrence of high O_3 concentrations at nonurban sites.

COMPARISON OF FIELD OBSERVATIONS WITH SMOG CHAMBER RESULTS

The following comparisons of smog chamber results with field observations will be made with data from a study conducted in the summer of 1974 (ref. 5) unless otherwise noted. The results of the field study were reported in Report EPA-450/3-75-036 entitled *Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies*.

The hourly averages of O_3 concentration for three rural sites are presented Figure 12. Hourly averages for NO_2 at the rural stations are presented in Figure 13 and hourly averages for NMHC are given in Figure 14.

In the field study, the NAAQS for photochemical oxidant was exceeded approximately twice as frequently at nonurban as at urban stations. In 1974, frequently the urban maxima were lower than the rural maxima, although in a few cases, the reverse was true.

All smog chamber data are presented in the various appendixes, and O_3 data from one run are presented in Figure 15 for easy comparison with the field data.

The experimental conditions for the first day of each chamber run were designed to represent the urban atmosphere, and the second and third days were to represent transported, "aged" photochemical systems. In all cases studied, the O_3 generated on the first day was greater than that generated on subsequent days.

The analogy between chemical behavior on the first day of a smog chamber run and that observed in urban atmospheres is not good. The city O_3 maxima are low compared with the first-day chamber maxima. Although the city data were, on the average, slightly lower than the rural data, they were generally comparable in value. Second- and third-day chamber data were always lower than the first-day smog chamber O_3 concentrations.

When O_3 concentrations were high in the field study, the cities under observation were surrounded with an atmosphere more comparable to the contents of the smog chambers on the second or third day of a run. A great difference in the behavior of the two systems (urban and chamber) is that no additional reactants were added to the chambers after the initial charge. Urban air, on the other hand, even when moving into rural areas, continually receives fresh reactants.

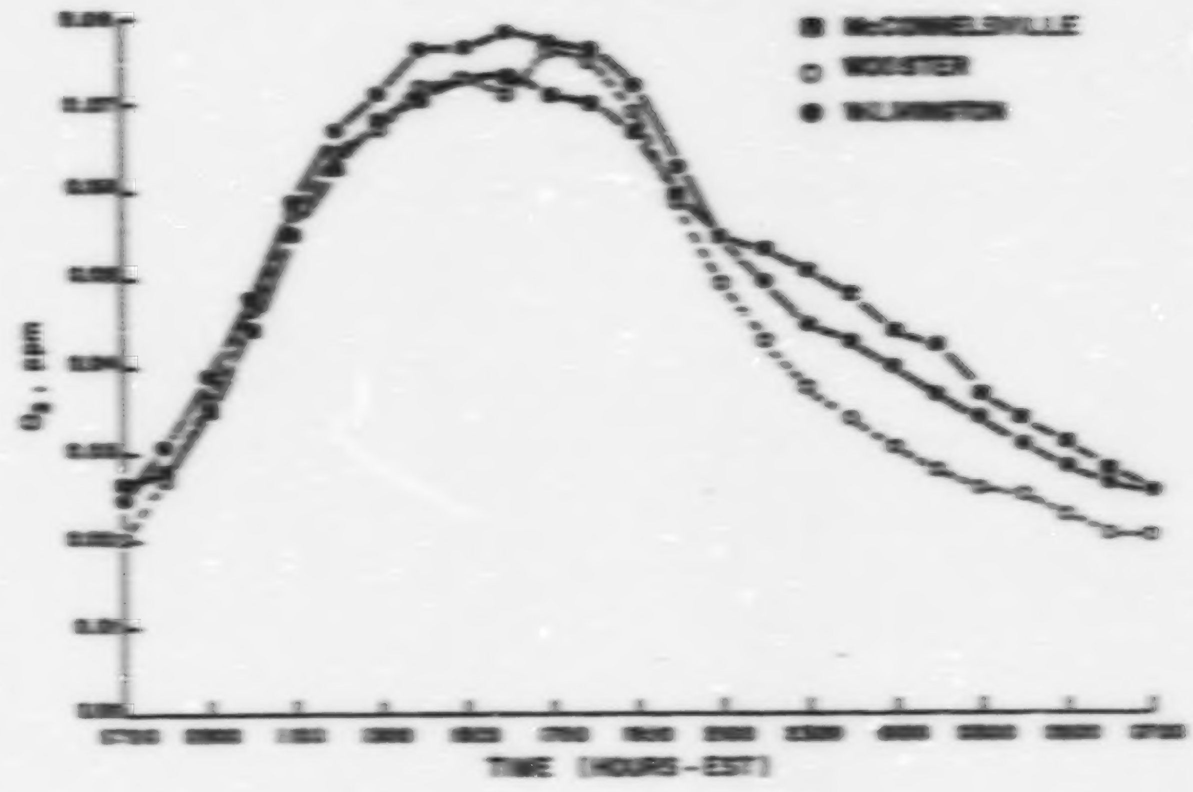

Figure 12. Mean diurnal O_3 concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 24–August 31, 1974.

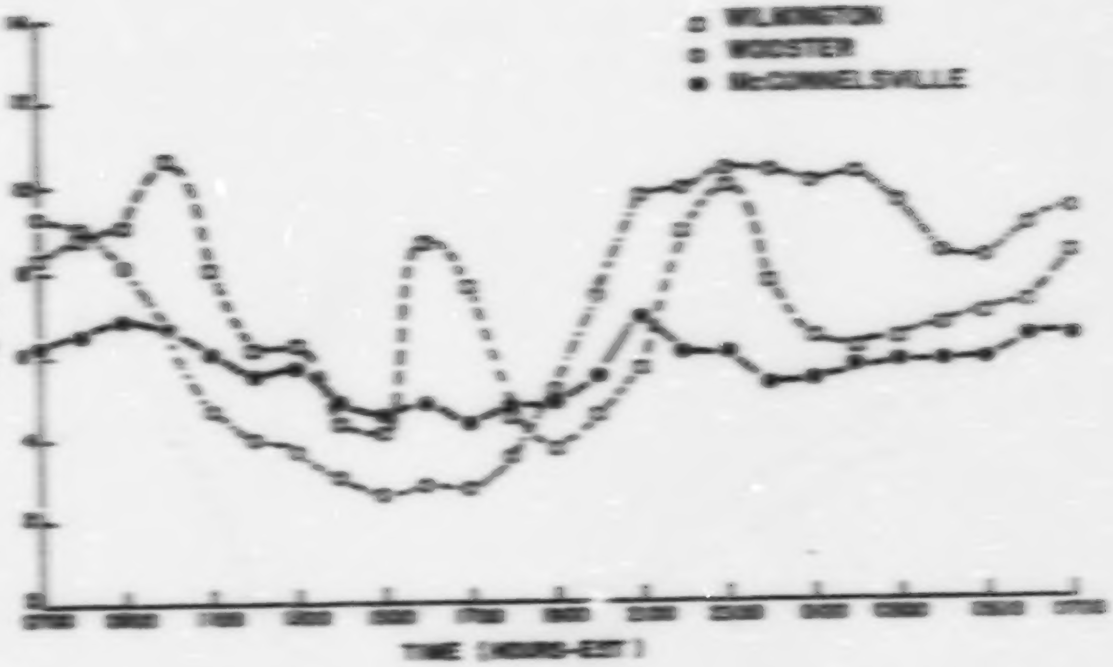

Figure 13. Mean diurnal NO_2 concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 15-August 31, 1974.

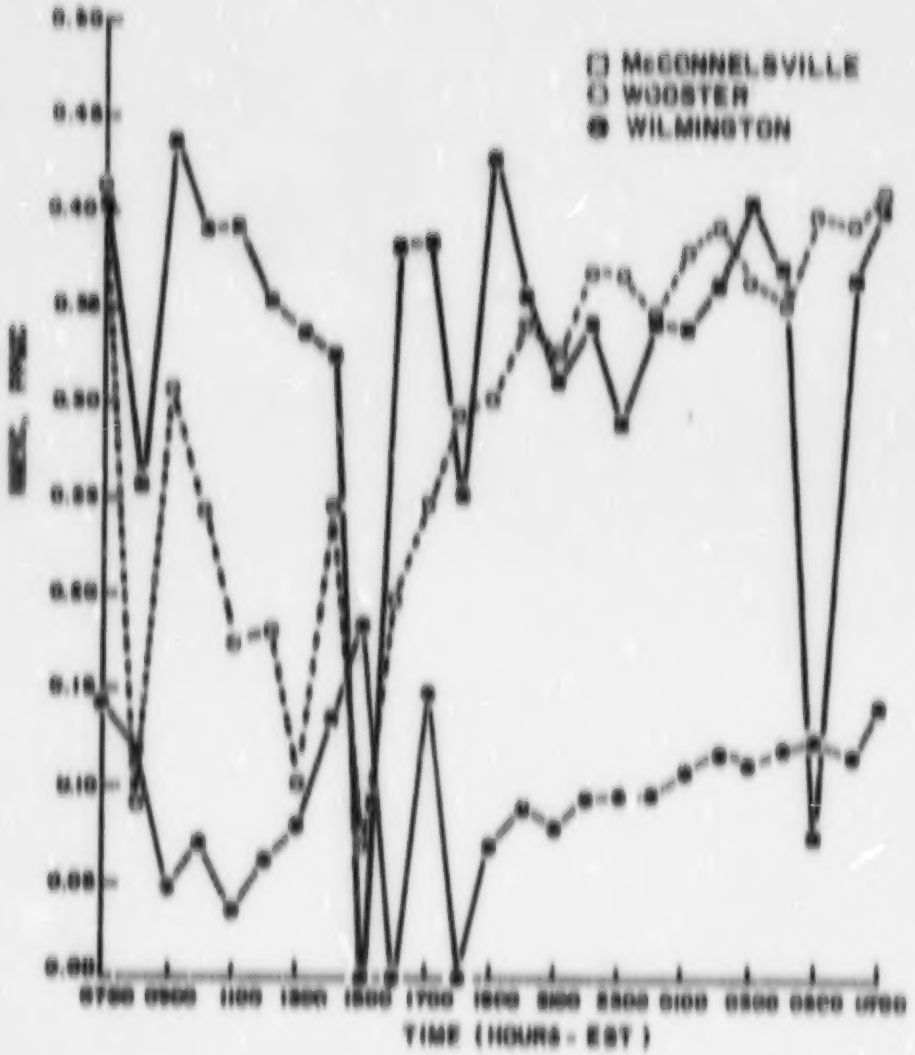

Figure 14. Mean diurnal NMHC concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 14-August 31, 1974.

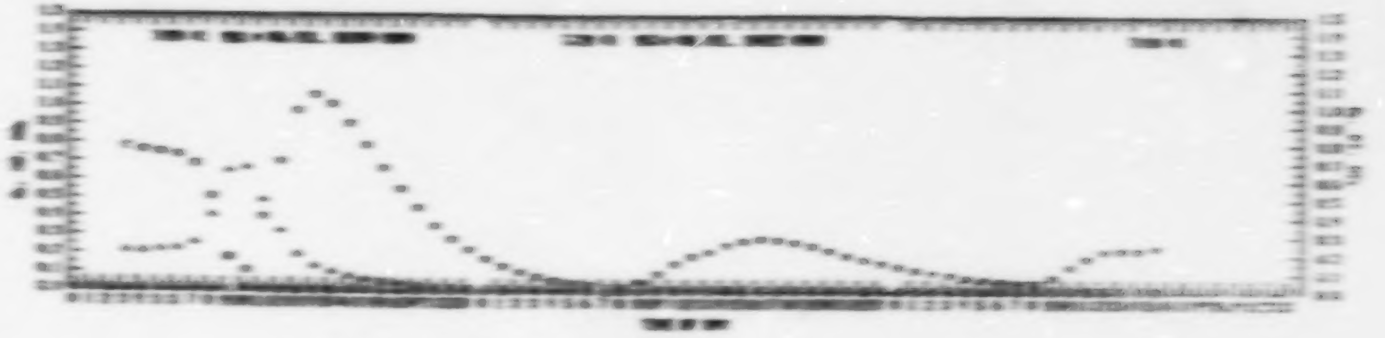

Figure 15. Typical three-day profiles for NO ([illegible]), NO_2 ([illegible]), and O_3 ([illegible]).

The closeness of the analogy between field data and second- and third-day chamber data, however, is surprisingly good. The average hourly concentrations of NO_2 at sunrise at five rural field sites were 5, 6, 6, 7, and 8 ppb. The chamber NO_x concentrations (only NO_2 was at concentrations high enough to register on the instrument) ranged from a measured 1 ppb to 39 ppb at sunrise on the second and third days of irradiation. Field NMHC concentrations at sunup at three stations were 0.15, 0.49 and 0.54 ppmC. Hydrocarbon/NO_x ratios were 25 $\frac{0.15}{.006}$, 61 $\frac{0.49}{.008}$, 108 $\frac{.54}{.005}$.

Most second- and third-day irradiations generated O_3 at concentrations above the NAAQS in the smog chambers. Examples of second- and third-day chamber data comparable to rural observations were $\frac{0.53}{0.014}$ $\frac{NMHC}{NO_x}$ (ratio 37) at sunrise producing a ΔO_3 of 0.18 ppm; $\frac{0.58}{0.007}$ (ratio 83) producing a ΔO_3 of 0.12 ppm; and $\frac{0.47}{0.004}$ (ratio 117) producing a ΔO_3 of 0.12 ppm.

The point of the above comparison is that O_3 in concentrations above the NAAQS can be generated in smog chambers from precursor concentrations (and ratios) similar to those found in the rural high O_3 situations.

Urban nocturnal concentrations were considerably higher at the rural sites than at the urban sites. Except when actual mechanical dilution was taking place, smog chamber O_3 concentrations never reached a measured zero at night. The explanation is that urban sources of NO are great enough to destroy the O_3 at night, while rural sources of O_3-destructive gases are too weak to destroy all the O_3. Thus, reduced levels of O_3-destructive precursors and reactive intermediates permit the overnight reduction of more than half of the chamber's O_3.

The retention of O_3 in nocturnal air is of importance in the total phenomenon of high O_3 concentrations in rural atmospheres. The smog chamber data obtained in this study can be used to begin to quantify the persistence of high nighttime O_3 concentrations in layers of air aloft in the lower troposphere. (See the previous discussion of nocturnal O_3 half-lives.)

Although the olefinic content of rural air was low, there was enough olefinic material to show that the sampled air had continually received fresh precursors. The olefinic concentration of the chamber air on the second and third day of irradiation is shown in Appendix A. Reduced olefinic content allows the accumulation of O_3 at low concentrations of NO_x and reduces the O_3-destructive capacity of the air.

In the RTI field study the NO_2 concentrations were low (e.g., hourly averages 1 to 10 ppb) and, as can be seen in Figure 13, there was little diurnal variation. Earlier studies involving high rural O_3 often did not report NO_x concentrations except to say they were "very low" (ref. 6).

In the chamber studies, the NO_2 concentrations "bottomed out" but never disappeared. These low NO_2 concentrations ranged from 1 to 39 ppb. While this might be construed to be an effect of chamber contamination by the original NO_x charge, it duplicates, on the second and third days of irradiation, the conditions observed in the field. The actual chemistry by which measureable concentrations of NO_2 could be maintained in the face of oxidation by O_3 and other oxidizing agents is not clear, but is sometimes speculated as being due to photolysis of nitroxy compounds other than nitrates. In the field it has been assumed to be due to continued low-level emissions. In chambers it has been assumed to be due to material sorbed by the walls at high initial reactant concentrations and desorbed later. In any event, the condition in the chambers simulated that in the field and may well represent some sort of cyclic gas-phase process in both cases.

Data from the RTI field study provide evidence which may indicate that local emissions were the major cause of the diurnal variation observed at rural sites. In the nocturnal radiation inversion these emissions may be equally as important as contact with the ground in causing the nighttime decrease of O_3. In the mornings they may mix with O_3 and the stable intermediates of the O_3 generation to form a system capable of O_3 generation. This interpretation is consistent with the vertical O_3 soundings depicted in Figure 10. The indicated diurnal O_3 curve between 600 and 1200 m is much shallower than the diurnal curve at ground level. This was interpreted as indicating that the air aloft, between 600 and 1200 m, had little O_3-generative or -destructive capacity. The fact that on the second and third day O_3 exhibits a diurnal curve in the chambers, where there were no added reactants, casts doubts on the assumed necessity of having local emissions. In other words, an "aged" photochemical system may contain sufficient O_3-generative capacity to exceed the standard. On the other hand, local pollutants, when present, will enter into both O_3-destruction and -generation processes.

Although the interpretation of field data may be correct, the "spent" photochemical system in the chamber is capable of considerable O_3 generation on second and third days of irradiation *without* the introduction of additional precursors *or* intermediates. The implication of this is that generation of O_3 and diurnal behavior similar to that observed in the field can, and in some cases may, occur in air drifting downwind of a city without any *local* emissions affecting the results.

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3. Intersociety Committee, Procedure 110, 1972. *Methods of Air Sampling and Analysis*. American Public Health Association, Washington, D.C.

4. Fox, D. L., Kamens, R., and Jeffries, H. E., 1975. Photochemical Smog Systems: Effect of Dilution on Ozone. *Science*, 188:No. 4193, p. 1113.

5. Research Triangle Institute, 1975. Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies. Environmental Protection Agency Publication No. EPA-450/3-75-036.

6. Research Triangle Institute, 1974. Investigation of Ozone and Ozone Precursor Concentrations at Nonurban Locations in the Eastern United States. Environmental Protection Agency Publication No. EPA-450/3-74-034.

APPENDIXES

Appendix A. INDIVIDUAL HYDROCARBON ANALYSES

Compound
Ethylene, ppbC
Propane, ppbC
Propylene, ppbC
Acetylene, ppbC
n-Butane, ppbC
1-Butene, ppbC
trans-2-Butene, ppbC
Isopentane, ppbC
Cyclopentane, ppbC
2-Methyl-2-Butene, ppbC
Toluene, ppbC
ortho-Xylene, ppbC
THC, ppmC
Methane, ppmC
Carbon Monoxide, ppmC
NMHC, ppmC

*In selected cases where analytical data are not available, estimates were made. Estimated concentrations are enclosed by parentheses.

Dilution 95%, Initiated at 1700 Dates: 7/22 - 7/24/75 Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0508	1615	0536	1705	0533	1646
Ethylene	---	116.8	3.85	3.7	2.09	1.08
Propane	---	369.0	23.03	21.39	18.82	11.43
Propylene	---	9.21	(3.0)	1.85	1.61	1.49
Acetylene	---	2.6	0.0	0.0	0.45	0.11
n-Butane	---	696.0	37.34	35.48	30.20	10.44
1-Butene	---	1.36	0.0	(0.0)	0.0	0.0
trans-2-Butene						
Isopentane	---	331.5	14.72	16.75	11.72	3.47
Cyclopentane	---	8.25	0.0	0.29	0.0	0.40
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
ortho-Xylene						
THC (ppm)	11.55	5.16	1.83	1.36	1.27	[illegible]
Methane	0.10	0.16	0.06	0.16	0.20	0.27
Carbon Monoxide	8.59	9.10	1.48	0.39	0.31	0.43
NMHC	11.45	5.00	1.78	1.20	1.07	1.07

Dilution 95%, Initiated at 1700 Dates: 7/22 - 7/24/75 Chamber No. 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0518	1631	0544	1716	0541	1656
Ethylene	---	20.3	2.25	1.88	1.55	0.94
Propane	---	72.9	8.90	6.86	3.12	1.44
Propylene	---	1.19	0.16	0.59	0.47	0.43
Acetylene	---	0.33	0.0	0.0	0.0	0.0
n-Butane	---	342.80	9.52	9.84	8.57	2.96
1-Butene	---	0.6	0.0	0.0	0.0	0.0
trans-2-Butene						
Isopentane	---	227.5	4.73	6.93	3.54	5.35
Cyclopentane	---	6.0	0.0	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
ortho-Xylene						
THC	6.94	3.69	1.46	1.24	1.15	1.16
Methane	0.47	0.50	0.162	0.25	0.21	0.25
Carbon Monoxide	9.60	9.95	1.16	0.24	0.21	0.37
NMHC	6.47	3.20	1.30	0.99	0.94	0.91

Dilution 95%, Initiated at 1700 Dates: 7/22 - 7/24/75 Chamber No. 3

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0528	1728	0553	1731	0550	1711
Ethylene	---	---	2.13	2.62	3.08	4.54
Propane	---	---	6.48	5.58	3.26	3.45
Propylene	---	---	0.23	0.66	1.25	0.69
Acetylene	---	---	0.0	0.0	0.64	0.54
n-Butane	---	---	7.91	9.84	14.94	2.91
1-Butene	---	---	0.07	0.0	0.60	0.0
trans-2-Butene						
Isopentane	---	---	4.29	3.25	8.76	7.45
Cyclopentane	---	---	0.0	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
ortho-Xylene						
THC	4.71	3.32	1.28	1.14	1.10	---
Methane	0.60	0.60	0.10	0.22	0.22	---
Carbon Monoxide	0.90	0.44	1.19	0.26	0.21	---
NMHC	4.11	2.73	1.18	0.92	0.89	---

Dilution 95%, Initiated at 1700 Dates: 7/22 - 7/24/75 Chamber No. 4

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0558	1650	0555	1600	0557	1726
Ethylene	---	5.62	1.01	3.40	1.30	2.06
Propane	---	16.47	2.51	1.31	0.23	0.80
Propylene	---	0.23	0.0	0.39	0.36	0.59
Acetylene	---	0.11	0.0	0.0	0.14	0.20
n-Butane	---	30.32	5.66	2.62	2.52	1.10
1-Butene	---	0.0	0.0	0.0	0.0	0.12
trans-2-Butene						
Isopentane	---	17.25	3.07	1.27	2.49	0.16
Cyclopentane	---	0.0	0.0	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
ortho-Xylene						
THC	2.14	1.89	1.22	1.31	1.21	1.20
Methane	0.38	0.43	0.28	0.49	0.49	0.44
Carbon Monoxide	10.00	9.21	0.85	0.10	0.10	0.27
NMHC	1.76	1.45	0.95	0.82	0.72	0.76

Dilution 95%, Initiated at NO_x Crossover

Dates: 7/28 - 7/30/75

Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0501	1701	0538	1738	0536	1538
Ethylene	(660)	37.20	1.78	---	1.82	---
Propane	660.0	275.10	9.63	---	8.96	---
Propylene	309.0	15.42	0.26	---	0.38	---
Acetylene	1184.0	143.20	7.70	---	6.60	---
n-Butane	2344.0	616.0	16.66	---	11.30	---
1-Butene	152.4	0.0	0.0	---	0.0	---
trans-2-Butene						
Isopentane	1065.0	331.50	6.70	---	4.31	---
Cyclopentane	(79)	8.05	0.0	---	0.0	---
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
ortho-Xylene						
THC	7.52	2.10	0.98	0.70	---	0.91
Methane	0.50	0.25	0.14	0.13	---	0.15
Carbon Monoxide	9.05	2.96	0.53	0.44	---	0.57
NMHC	7.02	1.85	0.84	0.57	---	0.81

Dilution 95%, Initiated at NO_x Crossover

Dates: 7/28 - 7/30/75

Chamber No. 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0517	1711	0545	1748	0544	1548
Ethylene	370.01	4.22	2.22	----	1.43	----
Propane	188.10	9.63	4.35	----	1.58	----
Propylene	420.0	0.0	0.35	----	0.35	----
Acetylene	130.80	0.60	0.0	----	0.0	----
n-Butane	1348.0	20.92	10.58	----	4.72	----
1-Butene	58.80	0.0	0.0	----	0.0	----
trans-2-Butene						
Isopentane	1025.0	12.65	2.42	----	1.30	----
Cyclopentane	26.70	0.0	0.0	----	0.0	----
2-Methyl-2-Butene						
Toluene	----	----	----	----	----	----
ortho-Xylene						
THC	4.81	1.50	1.07	0.87	----	0.99
Methane	0.57	0.47	0.35	0.20	----	0.32
Carbon Monoxide	10.00	2.20	0.22	0.24	----	0.30
NMHC	4.24	1.03	0.72	0.67	----	0.66

Dilution 95%, Initiated at NO_x Crossover Dates: 7/28 - 7/30/75 Chamber No. 3

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0527	1731	0554	1758	0552	1558
Ethylene	(384)	4.56	2.12	---	5.42	---
Propane	384.0	15.81	3.80	---	3.50	---
Propylene	117.30	0.32	0.51	---	0.55	---
Acetylene	596.0	0.0	0.0	---	0.66	---
n-Butane	1249.0	48.4	7.32	---	4.08	---
1-Butene	100.0	0.0	0.0	---	0.0	---
trans-2-Butene						
Isopentane	935.0	21.25	3.63	---	3.31	---
Cyclopentane	(37)	0.0	0.0	---	0.0	---
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
ortho-Xylene						
THC	4.05	1.07	0.60	0.35	---	0.66
Methane	0.10	0.09	0.08	0.10	---	0.10
Carbon Monoxide	8.93	2.55	0.31	0.33	---	0.43
NMHC	3.95	0.98	0.52	0.25	---	0.56

Dilution 95%, Initiated at NO_x Crossover   Dates: 7/28 - 7/30/75   Chamber No. 4

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0536	1731	0603	1828	0602	1628
Ethylene	98.40	5.90	1.04	---	3.13	---
Propane	82.35	15.18	0.66	---	1.11	---
Propylene	40.50	0.61	0.22	---	0.41	---
Acetylene	10.30	0.31	0.0	---	0.21	---
n-Butane	278.60	39.24	3.67	---	1.34	---
1-Butene	19.88	0.32	0.0	---	0.0	---
trans-2-Butene						
Isopentane	211.95	22.40	1.48	---	0.86	---
Cyclopentane	7.05	0.45	0.0	---	0.0	---
2-Methyl-2-Butene						
Toluene	---	---	---	---	---	---
Ortho-Xylene						
THC	2.05	1.25	1.00	0.94	---	1.15
Methane	0.90	0.65	0.40	0.41	---	0.58
Carbon Monoxide	10.00	2.02	0.20	0.23	---	0.34
NMHC	1.15	0.60	0.60	0.53	---	0.57

Dilution 77%, Initiated at NO_x Crossover   Dates: 8/4 - 8/6/75   Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0539	1801	0537	1601	0538	1638
Ethylene	0.83	1.10	0.58	0.0	---	---
Propane	12.75	2.64	4.83	0.96	---	---
Propylene	5.58	0.0	0.0	0.0	---	---
Acetylene	13.28	4.12	4.64	1.98	---	---
n-Butane	59.6	6.56	4.76	0.94	---	---
1-Butene	46.0	0.0	0.0	0.0	---	---
trans-2-Butene						
Isopentane	31.0	3.27	1.33	0.0	---	---
Cyclopentane	0.0	0.0	0.0	0.0	---	---
2-Methyl-2-Butene						
Toluene	770.0	183.4	144.2	21.07	---	---
ortho-Xylene						
THC	7.47	2.16	1.18	0.79	0.94	0.85
Methane	0.12	0.11	0.15	0.11	0.15	0.24
Carbon Monoxide	9.03	4.51	1.74	1.34	1.35	1.35
NMHC	7.35	2.05	1.03	0.68	0.79	0.67

Dilution 7/8, Initiated at NO_x Crossover

Dates: 8/4 - 8/6/75

Chamber 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0542	1811	0546	1611	0548	1648
Ethylene	7.82	0.62	0.43	0.27	---	---
Propane	12.57	0.73	---	0.36	---	---
Propylene	6.09	0.0	0.0	0.23	---	---
Acetylene	10.18	0.82	---	0.38	---	---
n-Butane	41.20	2.30	1.82	0.61	---	---
1-Butene	7.04	0.0	0.0	0.0	---	---
trans-2-Butene						
Isopentane	31.45	3.83	0.0	0.0	---	---
Cyclopentane	0.0	0.0	0.0	0.0	---	---
2-Methyl-2-Butene						
Toluene	1000.	124.6	67.87	8.89	---	---
ortho-Xylene						
THC	5.19	1.84	1.16	0.91	1.00	0.99
Methane	0.70	0.38	0.27	0.33	0.38	0.36
Carbon Monoxide	9.86	4.61	1.62	1.18	1.17	1.21
NMHC	4.41	1.46	0.89	0.58	0.62	0.63

Dilution 77%, Initiated at
NO_x Crossover

Dates: 8/4 - 8/6/75

Chamber 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0650	1021	0554	1650	0550	1650
Ethylene	---	1.05	0.37	---	---	---
Propane	---	8.46	1.75	---	---	---
Propylene	---	0.0	0.13	---	---	---
Acetylene	---	16.10	3.20	---	---	---
n-Butane	---	17.92	2.99	---	---	---
1-Butene	---	0.0	0.0	---	---	---
trans-2-Butene						
Isopentane	---	6.55	1.68	---	---	---
Cyclopentene	---	0.0	0.0	---	---	---
2-Methyl-2-Butene						
Toluene	---	156.8	1.32	---	---	---
ortho-Xylene						
THC (ppm)	4.50	1.59	0.83	0.71	0.81	0.84
Methane	0.11	0.15	0.22	0.09	0.26	0.36
Carbon Monoxide	9.03	3.86	1.28	0.96	0.89	0.89
NMHC	4.40	1.44	0.61	0.62	0.58	0.50

Dilution 77%, Initiated at NO_x Crossover

Dates: 8/4 - 8/6/75

Chamber No. 4

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0559	1831	0601	1631	0608	1608
Ethylene	1.63	0.71	0.51	0.0	---	---
Propane	3.0	1.79	0.56	0.0	---	---
Propylene	1.32	0.0	0.33	0.0	---	---
Acetylene	3.70	4.16	0.42	0.72	---	---
n-Butane	12.40	3.14	1.56	0.0	---	---
1-Butene	0.0	0.0	0.17	0.0	---	---
trans-2-Butene						
Isopentane	12.25	0.27	1.73	0.0	---	---
Cyclopentene	0.0	0.0	0.0	0.0	---	---
2-Methyl-2-Butene						
Toluene	295.4	50.82	0.6	0.0	---	---
ortho-Xylene						
THC (ppm)	1.14	0.85	0.87	0.70	0.70	0.73
Methane	0.14	0.10	0.17	0.08	0.26	0.35
Carbon Monoxide	10.34	3.87	1.33	1.04	0.93	0.89
NMHC	1.00	0.54	0.49	0.64	0.44	0.38

Dilution 77%, Initiated at NO_x Crossover　　Dates: 8/8 - 8/10/75　　Chamber No. 1

Compound	Time of Sample				
	Day 1		Day 2		Day 3
	0536	1731	0535	1540	0535
Ethylene	582.74	57.40	15.00	6.81	5.52
Propane	542.71	291.0	94.50	44.41	34.50
Propylene	197.90	9.54	2.24	1.49	1.03
Acetylene	744.01	312.0	95.00	49.66	30.40
n-Butane	1637.50	610.0	186.0	50.36	32.92
1-Butene	116.32	1.08	0.0	0.0	0.0
trans-2-Butene					
Isopentane	1152.40	324.0	95.50	21.16	17.30
Cyclopentane	27.28	7.25	2.11	0.45	0.0
2-Methyl-2-Butene					
Toluene	2021.5	625.10	(200)	59.99	58.45
ortho-Xylene					
THC (ppm)	7.05	3.88	2.10	---	1.72
Methane	1.23	1.19	1.18	---	1.20
Carbon Monoxide	8.48	5.13	1.70	---	1.31
NMHC	5.81	2.09	0.92	---	0.52

Dilution 77%, Initiated at NO_x Crossover Dates: 8/8 - 8/10/75 Chamber No. 2

Compound	Time of Sample				
	Day 1		Day 2		Day 3
	0546	1741	0543	1551	0543
Ethylene	288.15	26.60	10.88	1.74	2.54
Propane	294.89	122.70	42.30	12.06	10.59
Propylene	104.61	1.26	1.31	0.96	0.36
Acetylene	452.0	168.20	50.80	12.57	13.26
n-Butane	830.69	255.20	86.40	15.25	12.96
1-Butene	47.76	0.22	---	0.0	0.0
trans-2-Butene					
Isopentane	535.16	134.50	46.15	9.82	6.60
Cyclopentane	14.62	3.21	1.12	0.0	0.0
2-Methyl-2-Butene					
Toluene	1308.30	390.60	200.20	41.86	22.40
ortho-Xylene					
THC (ppm)	3.64	1.39	0.72	---	0.69
Methane	0.13	0.11	0.20	---	0.07
Carbon Monoxide	10.25	4.99	1.65	---	0.97
NMHC	3.52	1.28	0.52	---	0.62

Dilution 7/7, Initiated at NO_x Crossover

Dates: 8/8 - 8/10/75

Chamber No. 3

Compound	Time of Sample				
	Day 1		Day 2		Day 3
	0552	1748	0552	1558	0551
Ethylene	249.73	36.40	11.58	3.63	6.40
Propane	249.51	98.70	42.0	11.19	17.01
Propylene	92.70	1.88	1.76	1.06	1.02
Acetylene	315.68	115.20	44.20	10.68	13.94
n-Butane	731.56	230.40	87.60	13.97	14.68
1-Butene	38.94	0.36	0.0	0.0	0.0
trans-2-Butene					
Isopentane	458.35	129.0	46.55	7.36	7.30
Cyclopentane	12.27	4.24	0.97	0.0	0.0
2-Methyl-2-Butene					
Toluene	1050.26	196.70	108.50	36.33	25.62
ortho-Xylene					
THC (ppm)	3.24	1.38	0.69	---	0.91
Methane	0.15	0.12	0.14	---	0.07
Carbon Monoxide	8.80	4.41	1.33	---	0.86
NMHC	3.09	1.28	0.55	---	0.84

Dilution 77%, Initiated at NO$_x$ Crossover   Dates: 8/8 - 8/10/75   Chamber No. 4

Compound	Time of Sample				
	Day 1		Day 2		Day 3
	0800	1751	0602	1606	0800
Ethylene	61.70	10.12	4.46	5.36	3.14
Propane	54.22	26.31	8.04	4.54	2.81
Propylene	20.21	1.50	0.35	1.39	0.38
Acetylene	39.78	18.50	6.12	1.24	1.88
n-Butane	149.34	54.0	22.56	7.82	5.40
1-Butene	10.17	0.0	0.0	0.90	0.0
trans-2-Butene					
Isopentane	82.29	29.15	12.70	8.52	4.02
Cyclopentane	0.89	0.0	0.0	0.0	0.0
2-Methyl-2-Butene					
Toluene	261.10	149.80	73.50	42.0	45.22
ortho-Xylene					
THC (ppm)	1.04	0.55	0.68	---	0.99
Methane	0.11	0.13	0.13	---	0.28
Carbon Monoxide	10.46	4.92	1.53	---	1.08
NMHC	0.93	0.41	0.55	---	0.71

Dilution Static Dates: 8/12 - 8/16/75 Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0536	1631	0536	1638	0538	1538
Ethylene	557.12	83.6	---	---	---	---
Propane	449.85	360.0	---	---	---	---
Propylene	180.71	0.0	---	---	---	---
Acetylene	415.05	336.0	---	---	---	---
n-Butane	946.52	848.0	---	---	---	---
1-Butene	112.75	0.0	---	---	---	---
trans-2-Butene						
Isopentane	1115.80	865.0	---	---	---	---
Cyclopentane	33.83	24.9	---	---	---	---
2-Methyl-2-Butene						
Toluene	2086.50	959.0	---	---	---	---
ortho-Xylene						
THC	9.02	5.93	5.05	4.33	4.23	3.82
Methane	1.29	1.14	1.22	1.22	1.20	1.27
Carbon Monoxide	8.70	8.58	9.09	8.89	8.52	8.47
NMHC	7.73	4.79	3.83	3.11	3.04	2.55

Dilution Static | Dates: 8/12 - 8/15/75 | Chamber No. 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0545	1641	0548	1748	0548	1548
Ethylene	302.81	74.6	---	---		---
Propane	246.48	217.5	---	---	---	---
Propylene	92.62	3.1	---	---	---	---
Acetylene	203.90	169.8	---	---	---	---
n-Butane	538.54	384.8	---	---	---	---
1-Butene	61.74	0.0	---	---	---	---
trans-2-Butene						
Isopentane	503.78	325.0	---	---	---	---
Cyclopentane	15.51	8.8	---	---	---	---
2-Methyl-2-Butene						
Toluene	482.02	---	---	---	---	---
ortho-Xylene						
THC	4.94	3.38	3.30	2.82	2.73	2.60
Methane	0.60	0.52	0.69	0.56	0.71	0.69
Carbon Monoxide	9.50	9.61	9.89	9.58	9.30	8.93
NMHC	4.34	2.85	2.60	2.25	2.02	1.91

Dilution Static Dates: 8/13 - 8/15/75 Chamber No. 3

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0554	1649	0558	1758	0558	1558
Ethylene	264.14	47.2	---	---	---	---
Propane	201.61	126.0	---	---	---	---
Propylene	81.02	2.3	---	---	---	---
Acetylene	172.29	99.4	---	---	---	---
n-Butane	496.79	247.6	---	---	---	---
1-Butene	54.12	0.0	---	---	---	---
trans-2-Butene						
Isopentane	510.10	300.0	---	---	---	---
Cyclopentane	16.59	10.8	---	---	---	---
2-Methyl-2-Butene						
Toluene	851.06	497.7	---	---	---	---
ortho-Xylene						
THC	3.97	2.55	2.55	2.00	2.08	1.80
Methane	0.16	0.10	0.08	0.11	0.28	0.39
Carbon Monoxide	8.76	8.65	8.19	7.65	6.98	6.40
NMHC	3.81	2.45	2.47	1.89	1.81	1.41

Dilution Static Dates: 8/12 - 8/14/75 Chamber No. 4

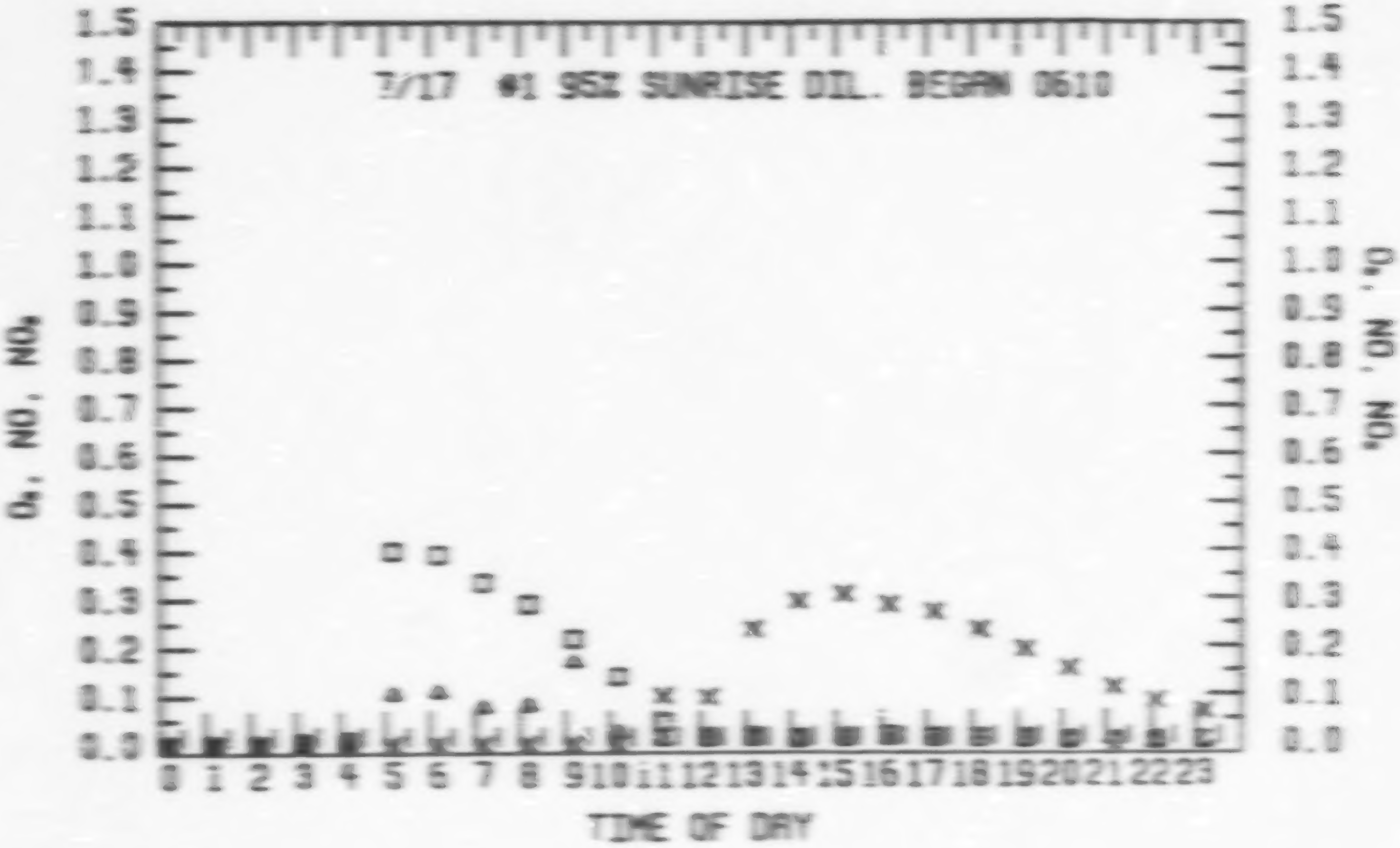
Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0602	1659	0601	1726	0602	1651
Ethylene	65.51	26.40	26.78	17.64	8.71	10.56
Propane	56.77	61.20	62.81	50.72	41.22	28.52
Propylene	23.99	1.06	2.76	3.21	1.83	1.00
Acetylene	42.83	47.0	47.40	35.86	27.60	27.86
n-Butane	110.92	110.80	134.04	93.98	83.84	61.70
1-Butene	13.21	0.0	0.0	0.0	0.0	0.0
trans-2-Butene						
Isopentane	124.39	92.0	92.05	56.3	50.63	33.94
Cyclopentane	3.61	2.33	2.34	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	276.86	—	106.69	75.91	—	53.91
ortho-Xylene						
THC	1.67	1.31	1.42	1.37	1.46	1.46
Methane	0.11	0.06	0.12	0.27	0.39	0.53
Carbon Monoxide	9.40	8.84	8.59	7.65	7.23	6.40
NMHC	1.56	1.25	1.30	1.10	1.07	0.93

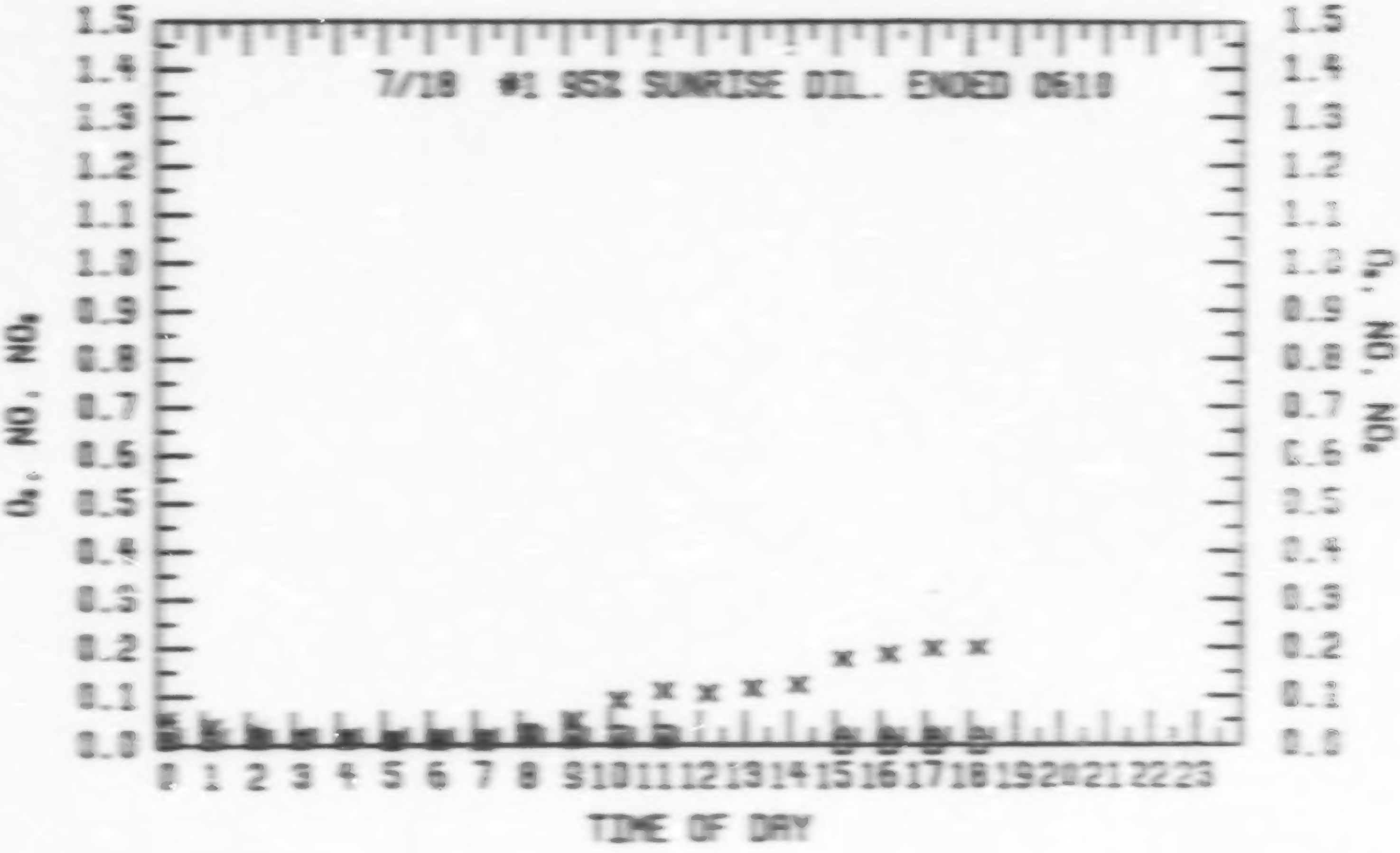
Appendix B. CONCENTRATION PROFILES

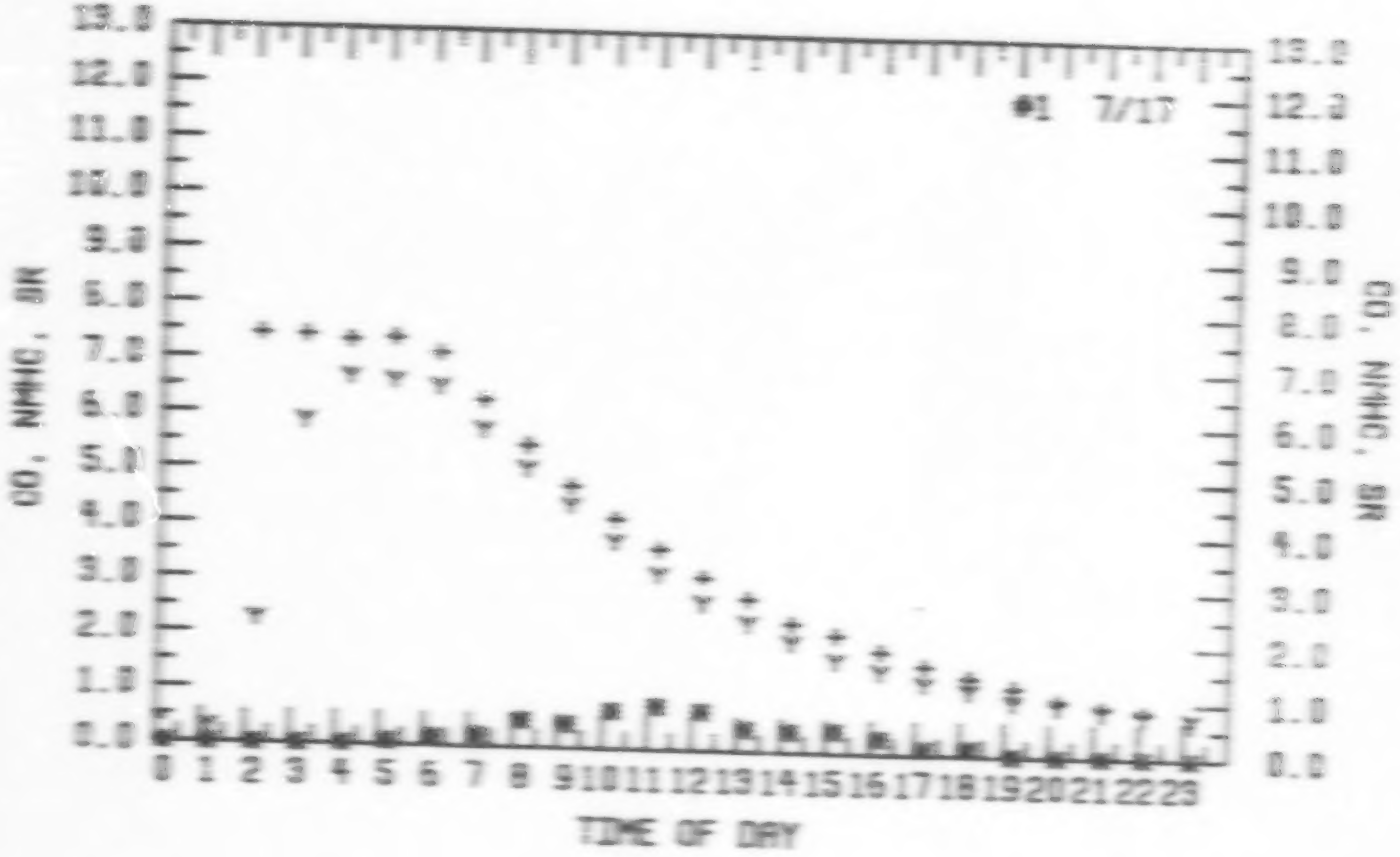
Symbols:

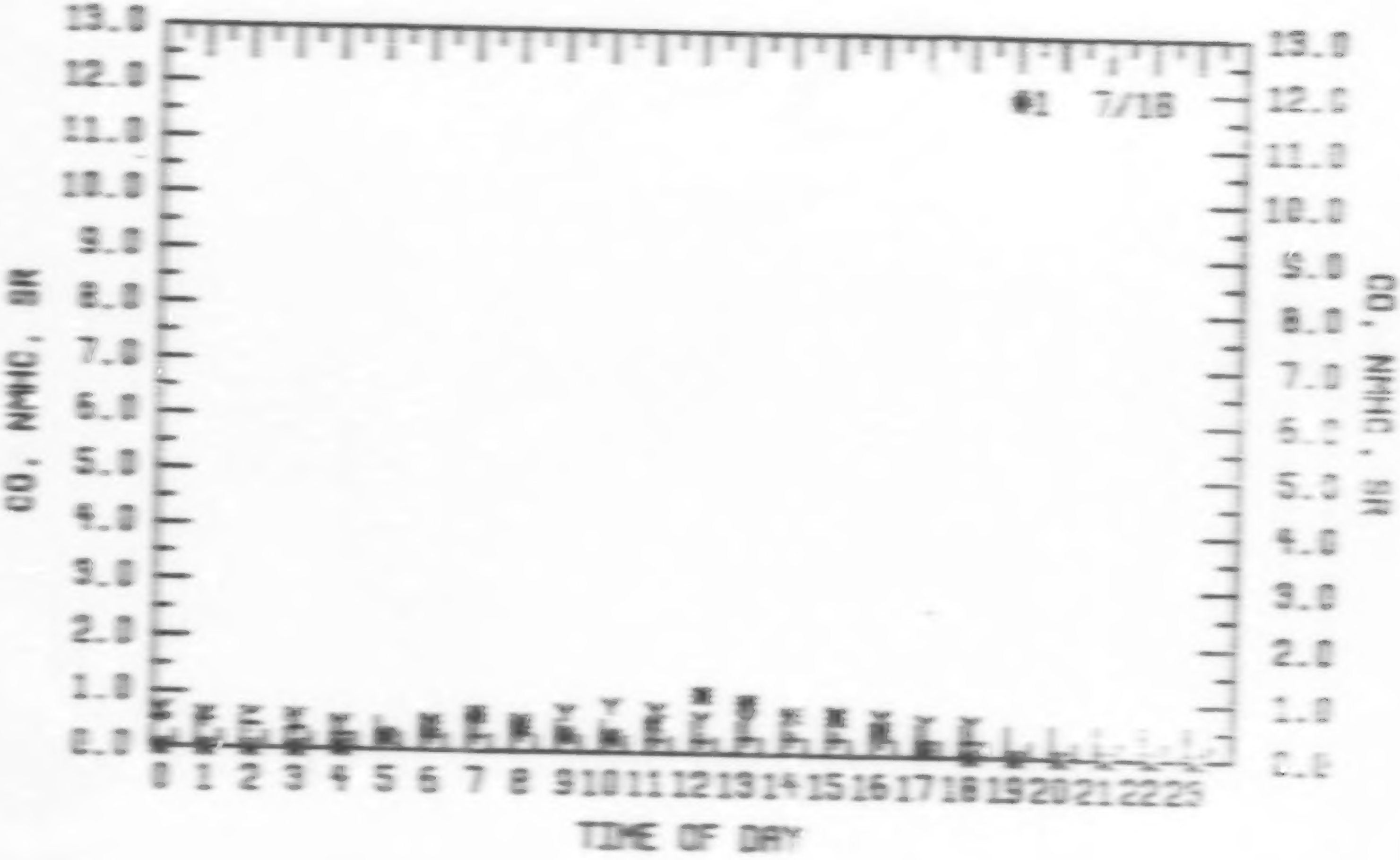
X	Ozone ppm
⊠	Nitric Oxide ppm
Δ	Nitrogen Dioxide ppm
♦	Carbon Monoxide ppm
Y	Nonmethane Hydrocarbon (ppmC)
*	Solar Radiation (Langleys per minute)

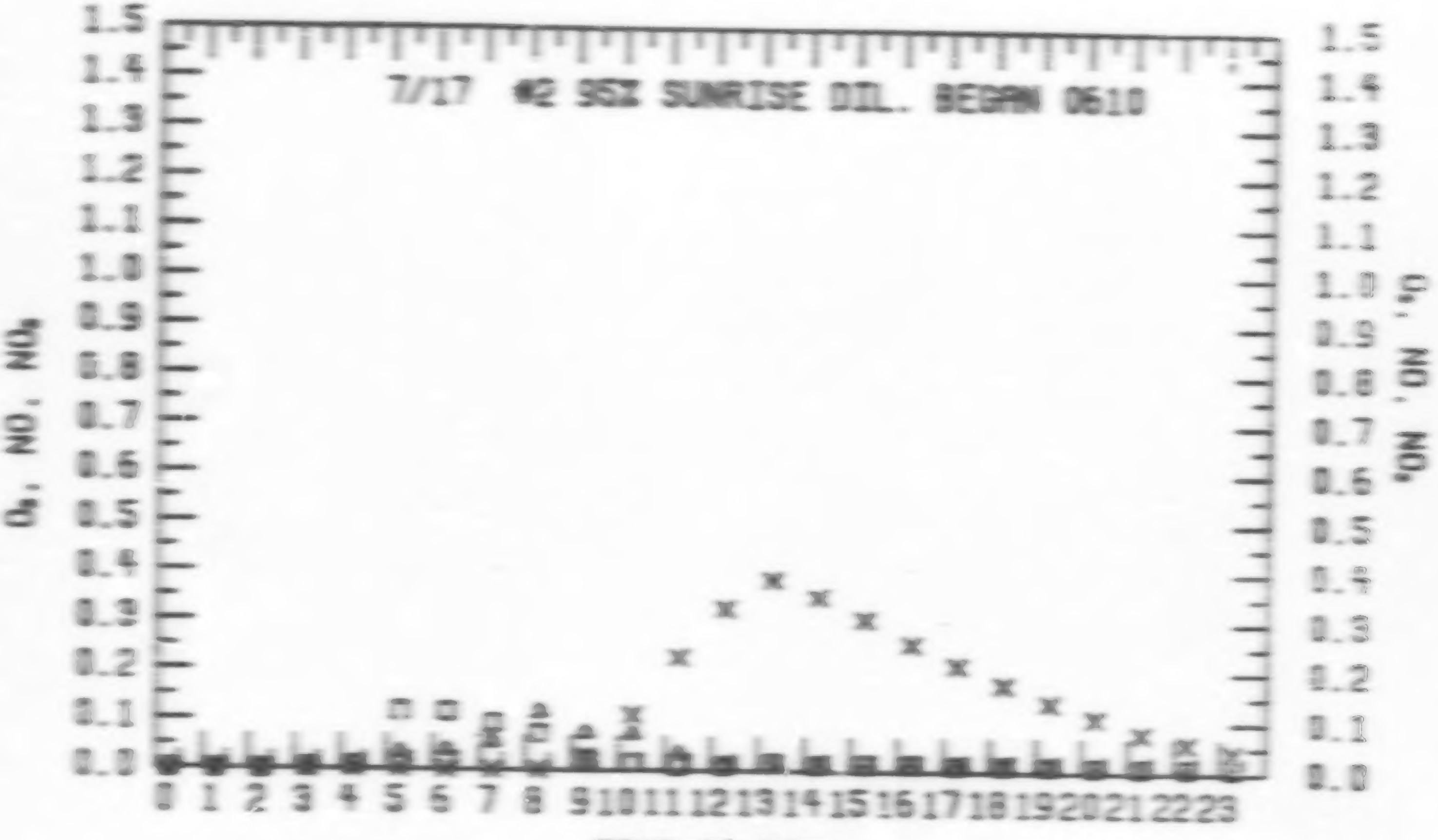
Dates, chamber numbers, percent dilution in 24 hours, and time dilution began are presented on the ozone graphs of the first two days.


7/17 #1 95% SUNRISE DIL. BEGAN 0610
O_3, NO, NO_2
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/18 #1 95% SUNRISE DIL. ENDED 0610
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#1 7/17
CO, NMHC, SR
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
#1 7/18
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/17 #2 95% SUNRISE DIL. BEGAN 0610
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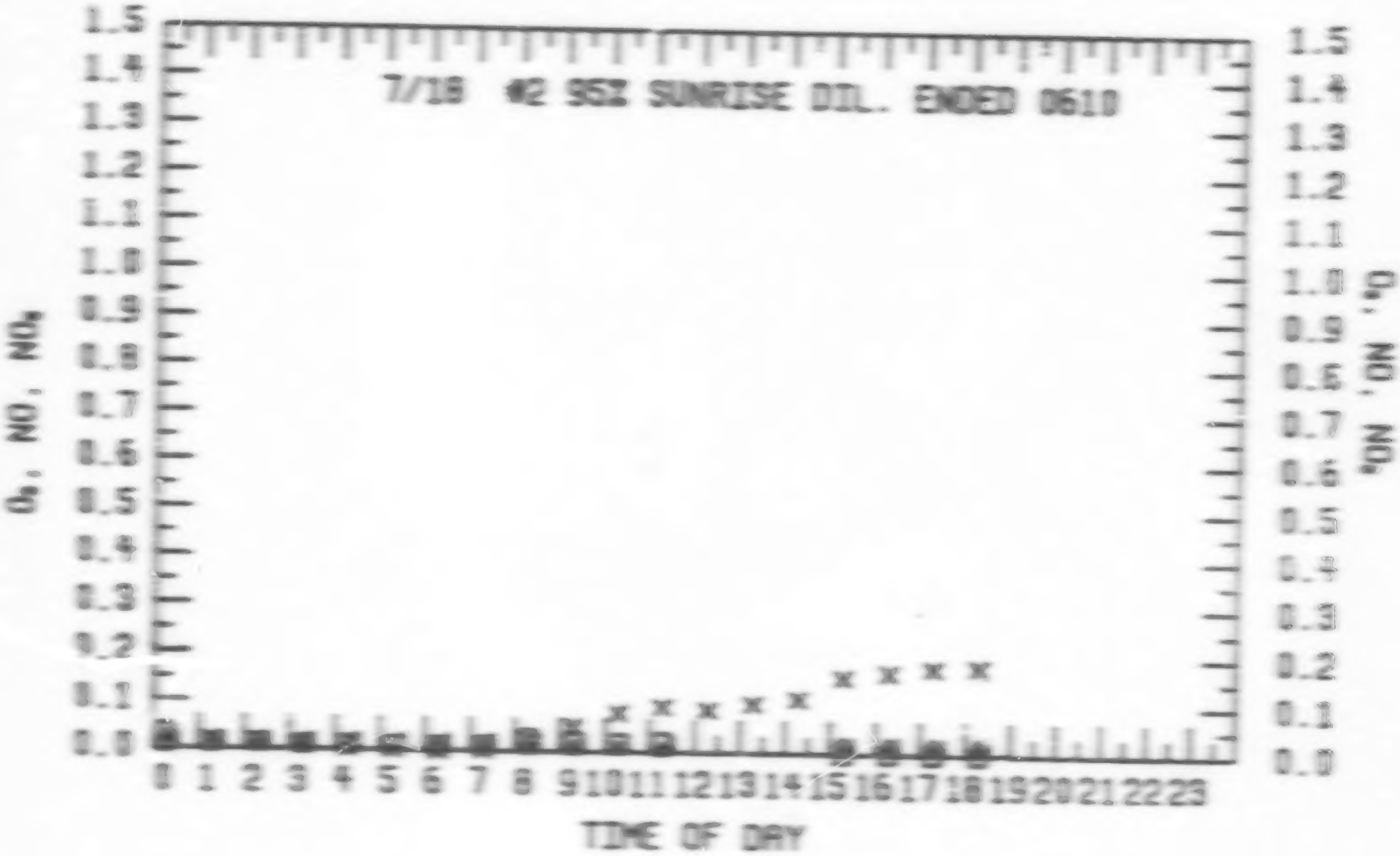
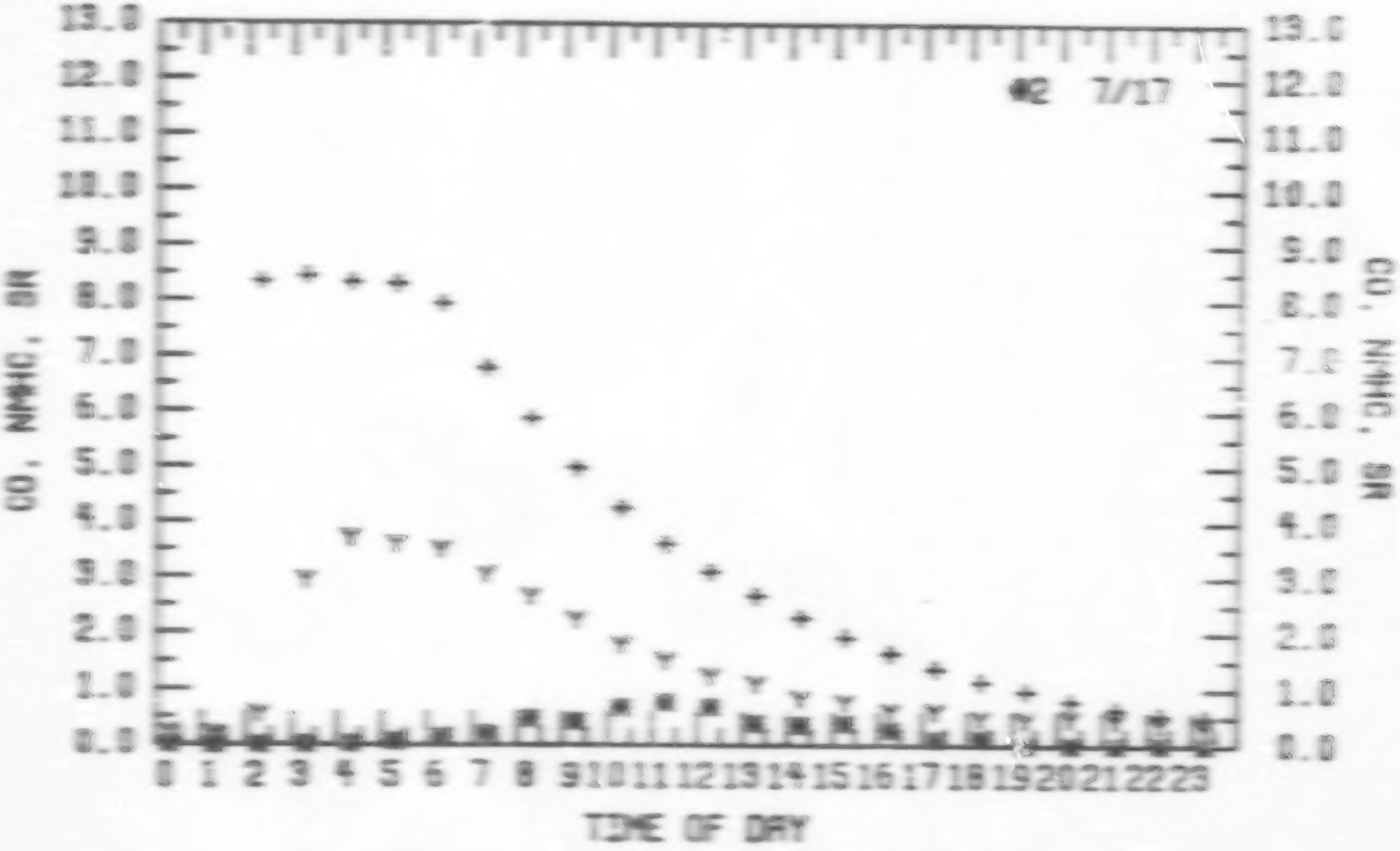
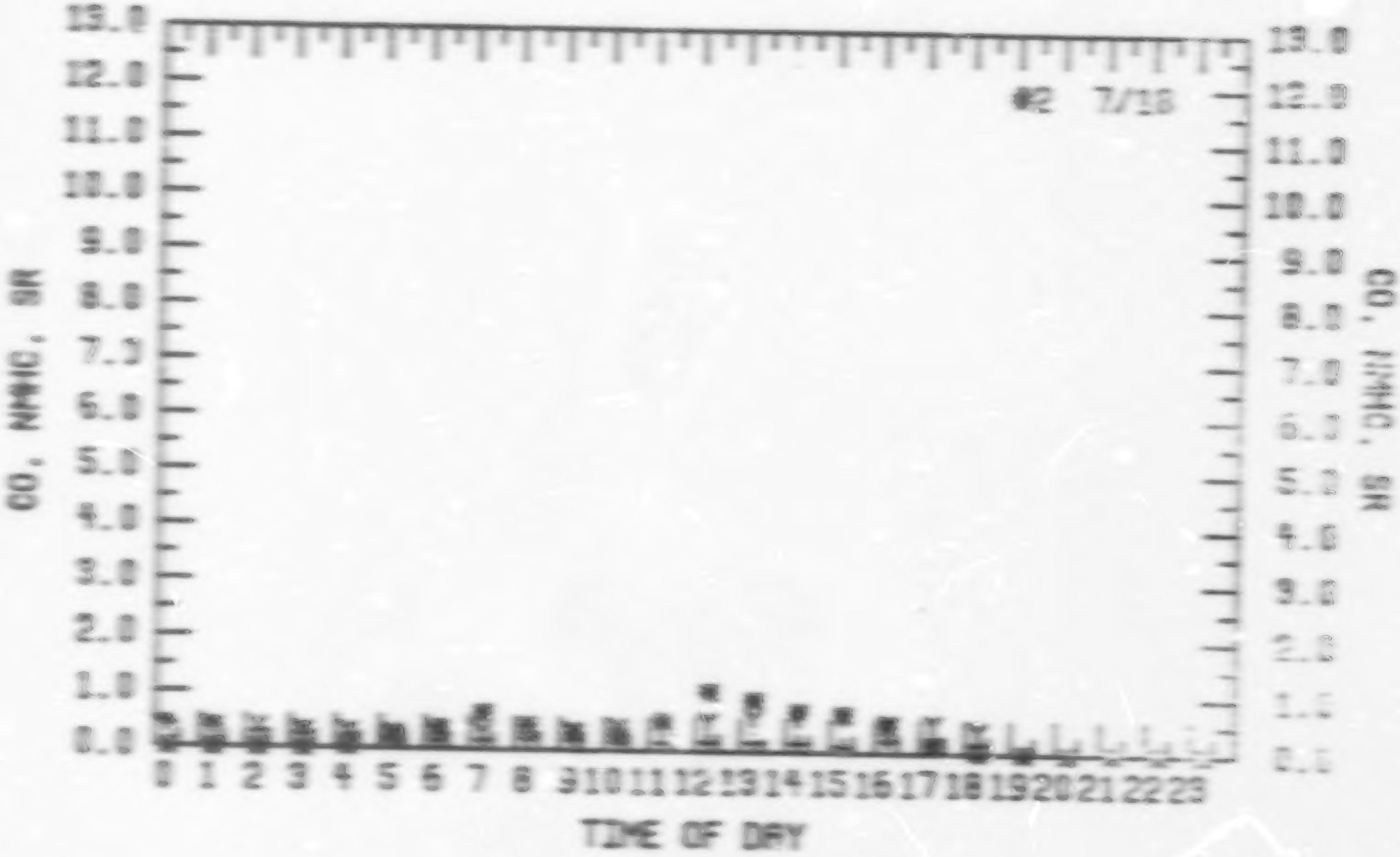
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/18 #2 95% SUNRISE DIL. ENDED 0610
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#2 7/17
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY



CO, NMHC, SR
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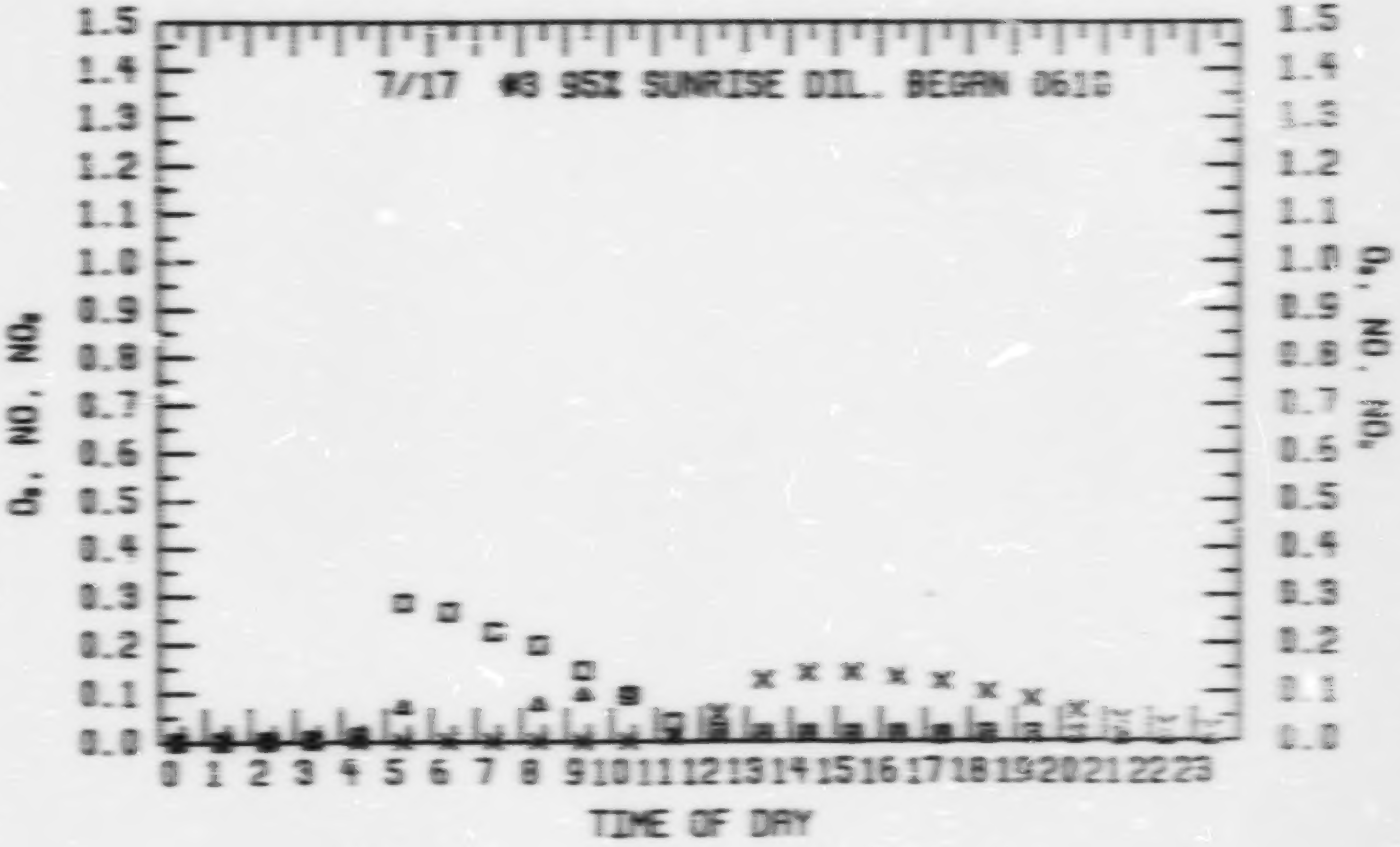
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#2 7/16
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/17 #3 95% SUNRISE DIL. BEGAN 0610
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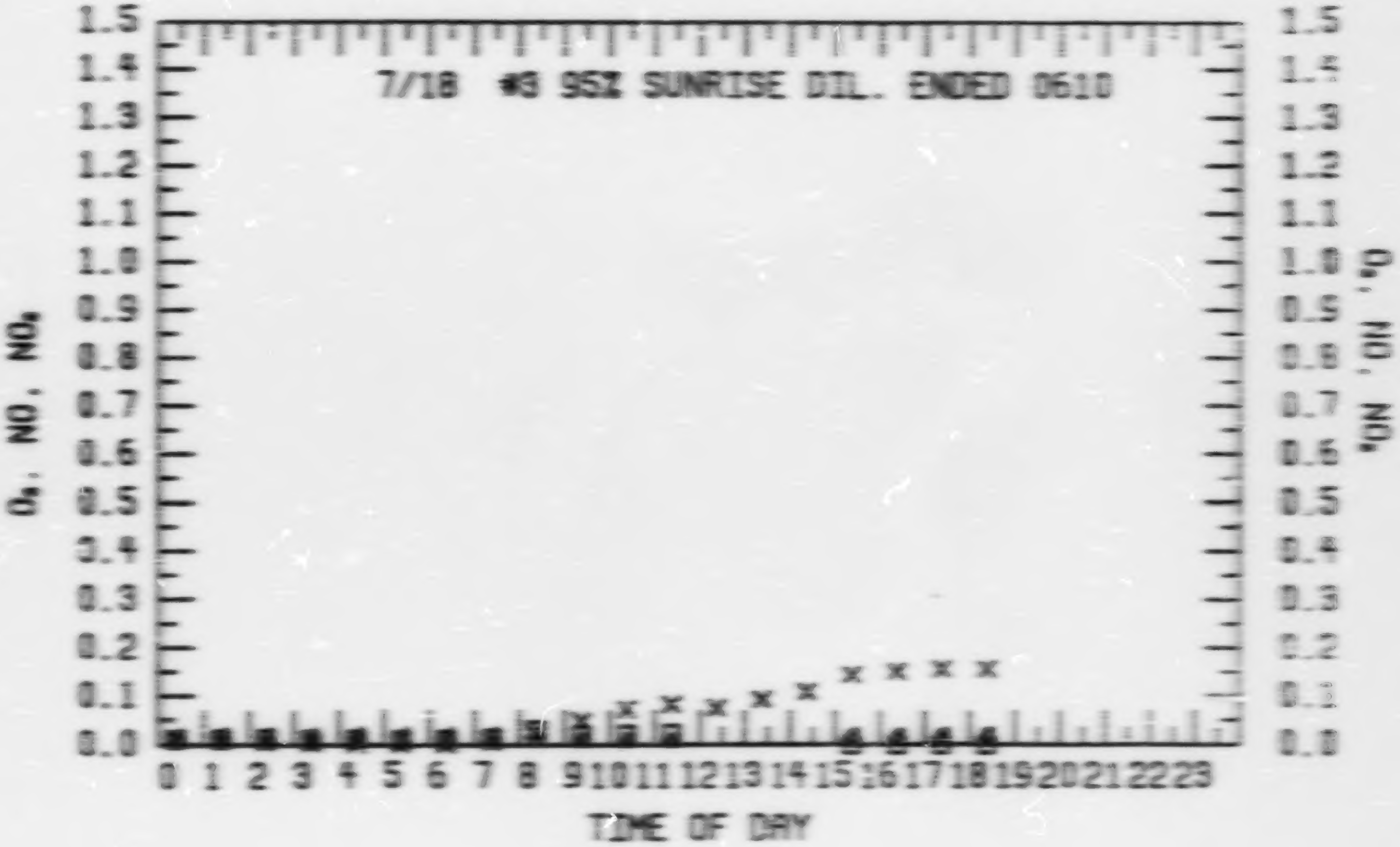
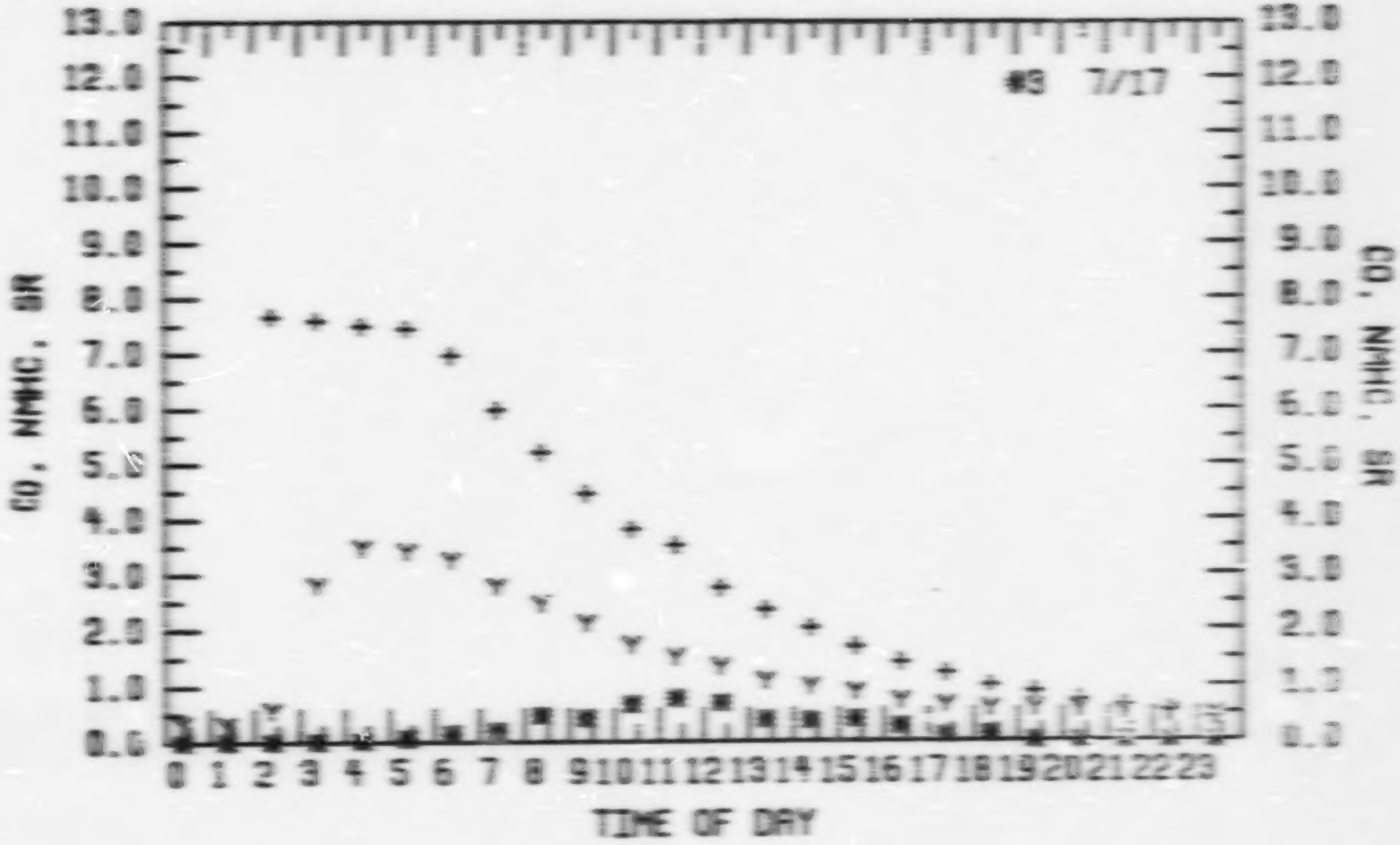
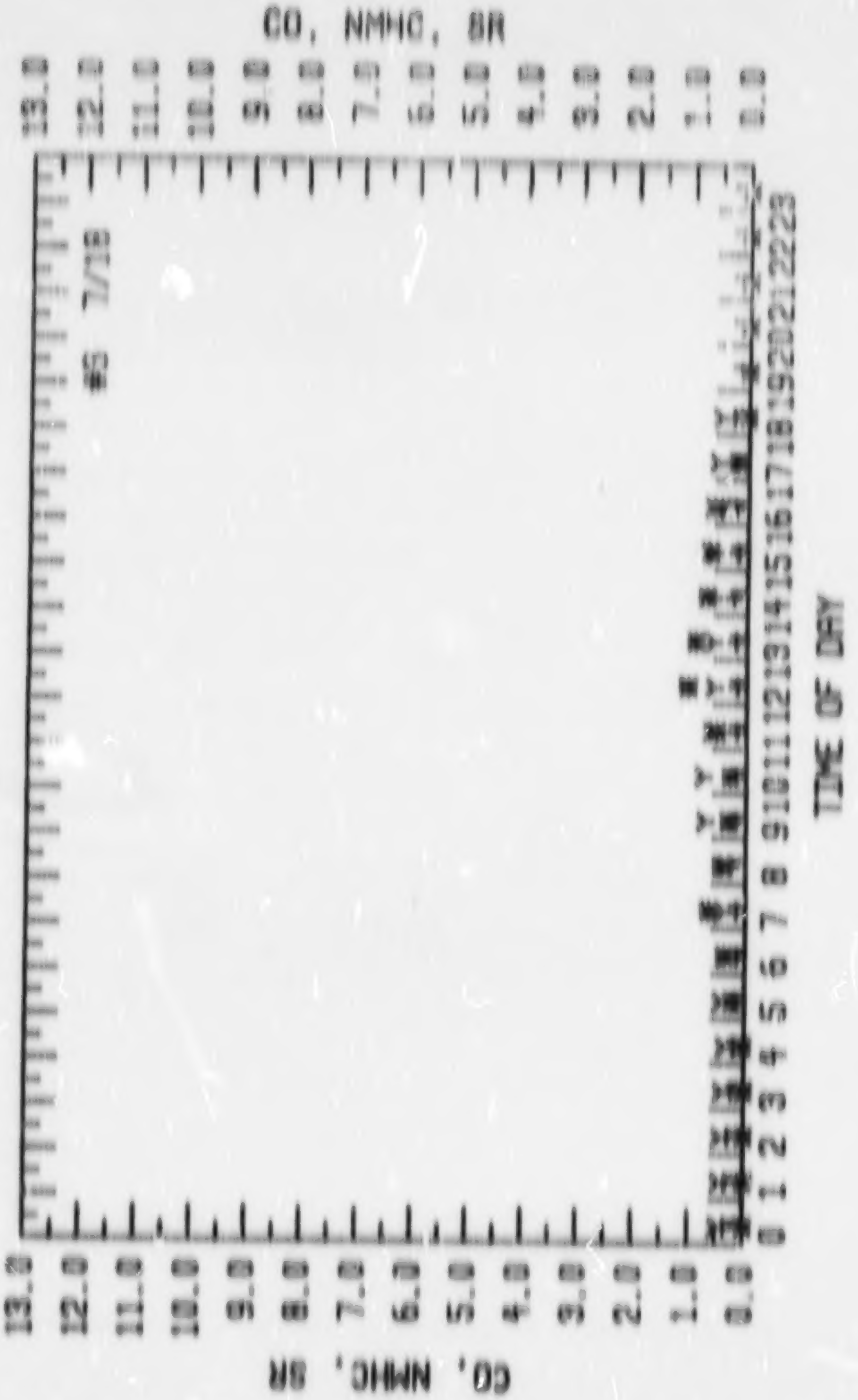
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

7/18 #3 95% SUNRISE DIL. ENDED 0610
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY



13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
#3 7/17
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#5 7/18
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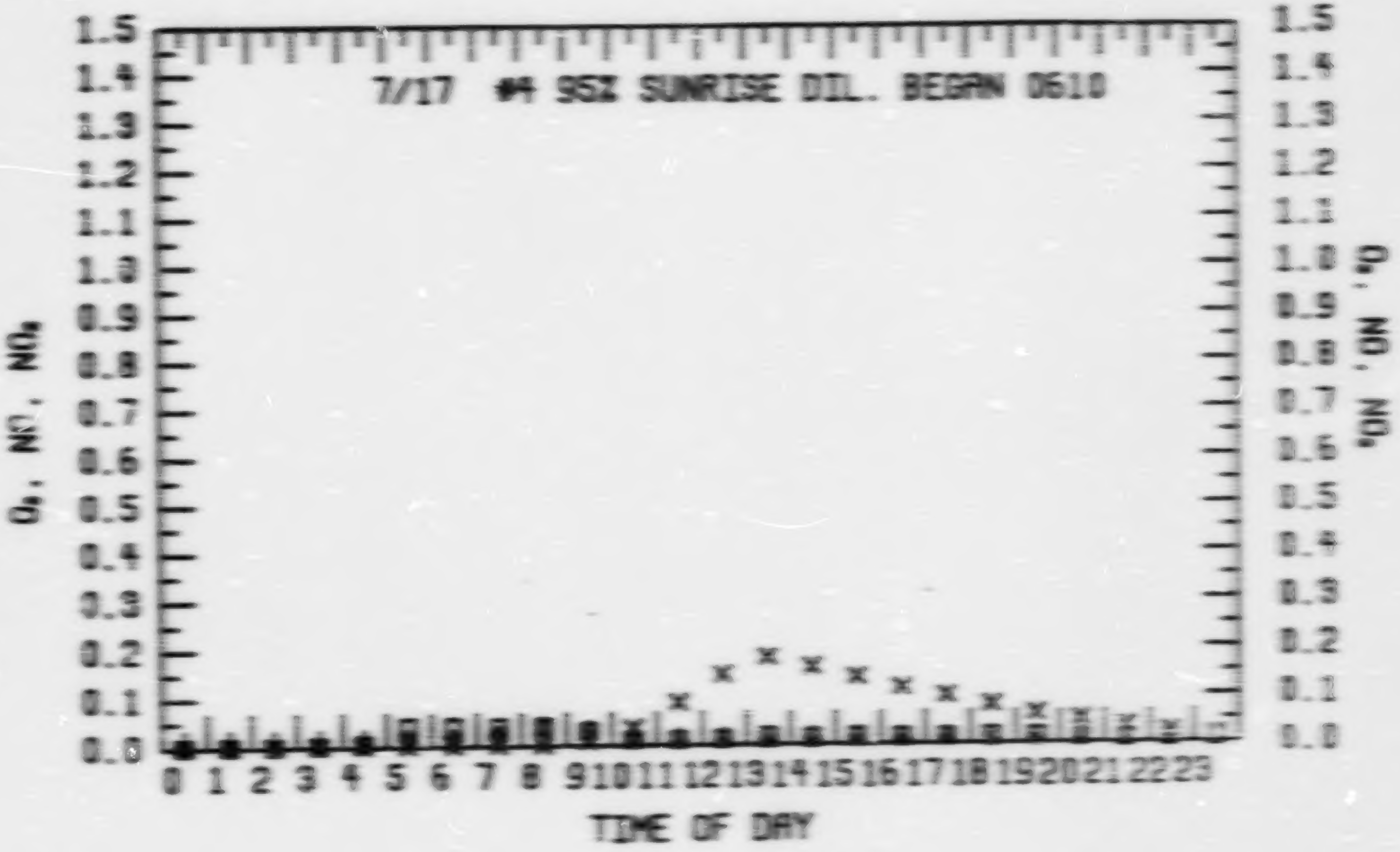
TIME OF DAY


7/17 #4 95% SUNRISE DIL. BEGAN 0610
O3, NO, NO2
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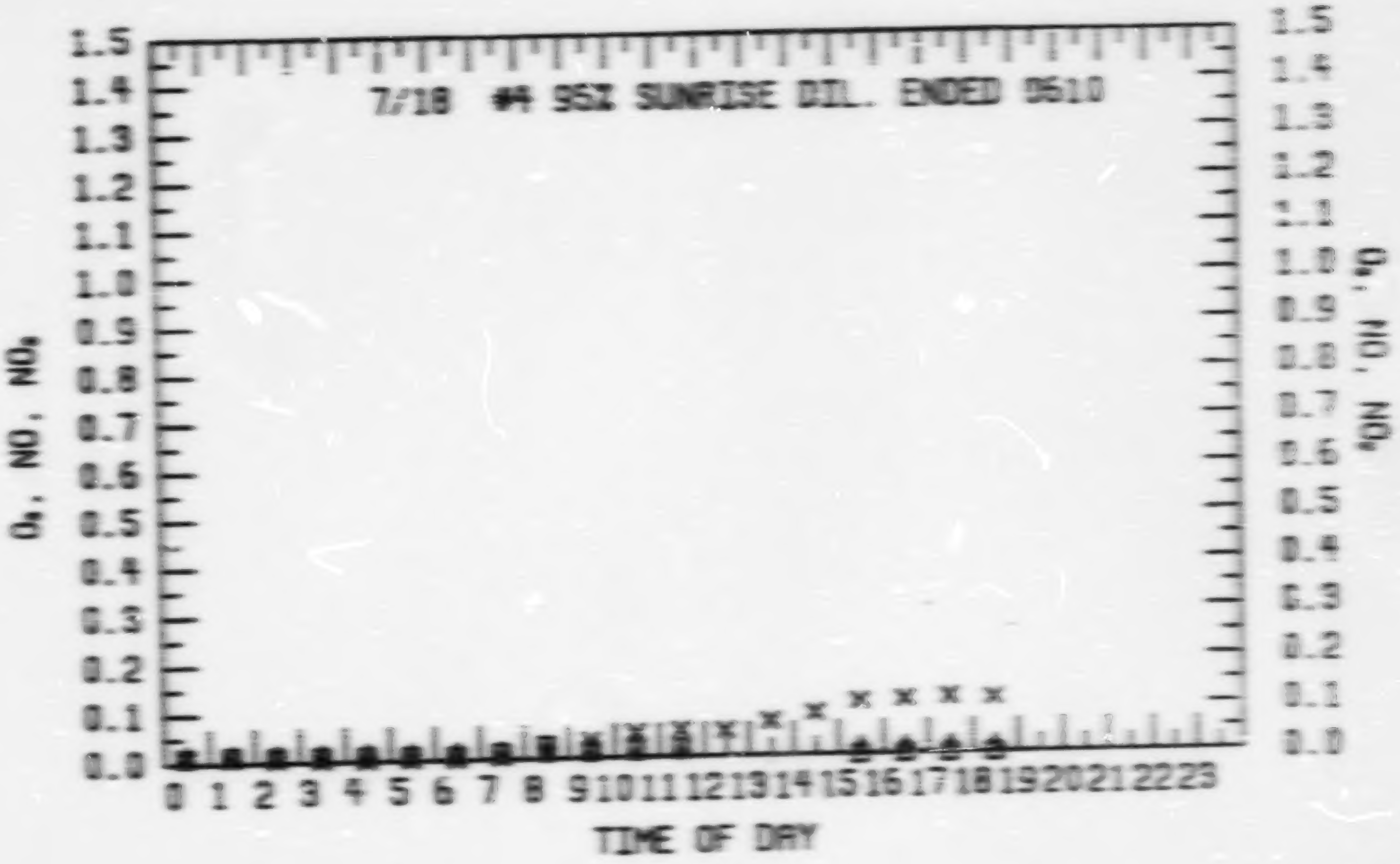
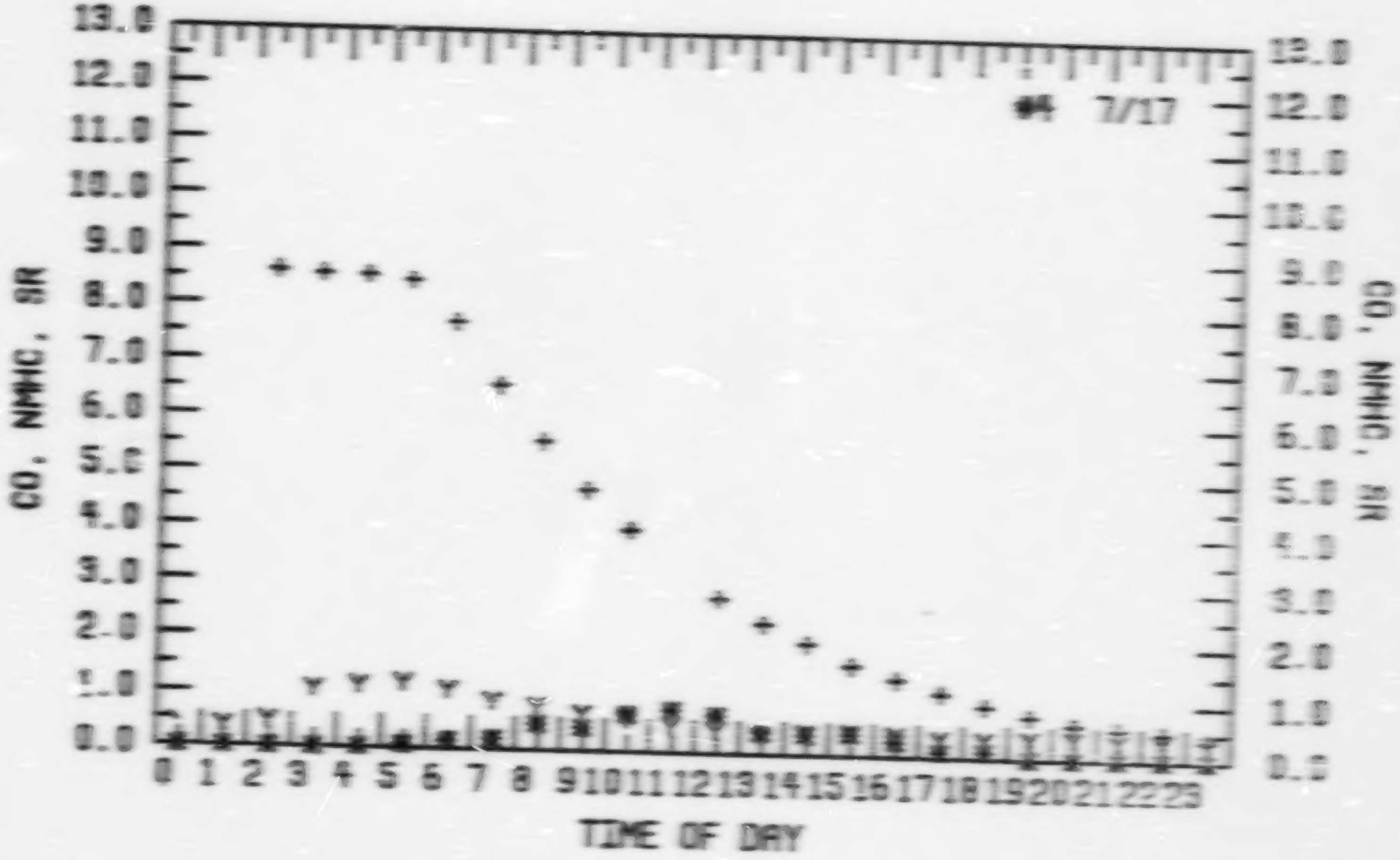
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/18 #4 95% SUNRISE DIL. ENDED 0510
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#4 7/17
CO, NMHC, SR
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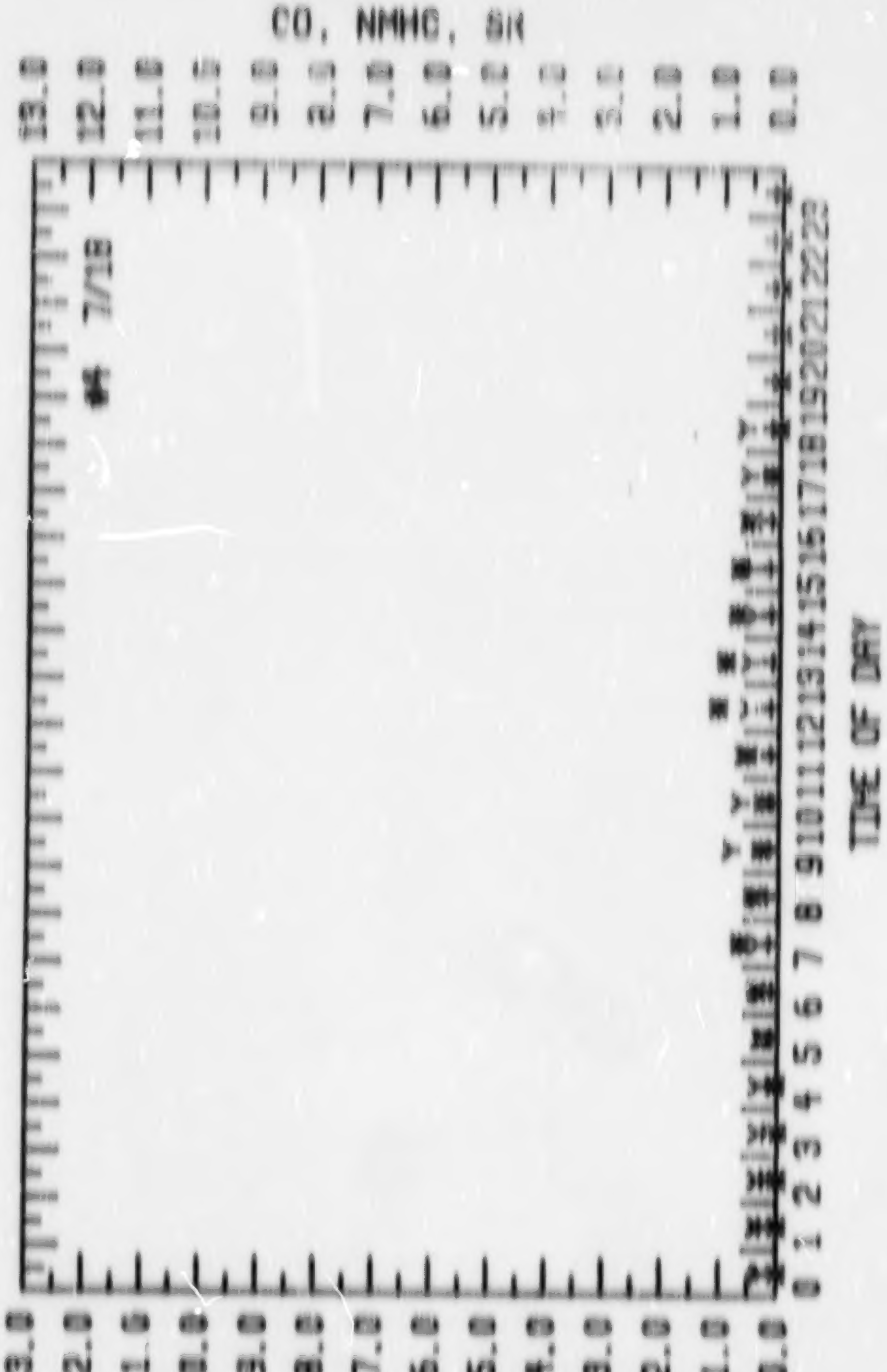
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
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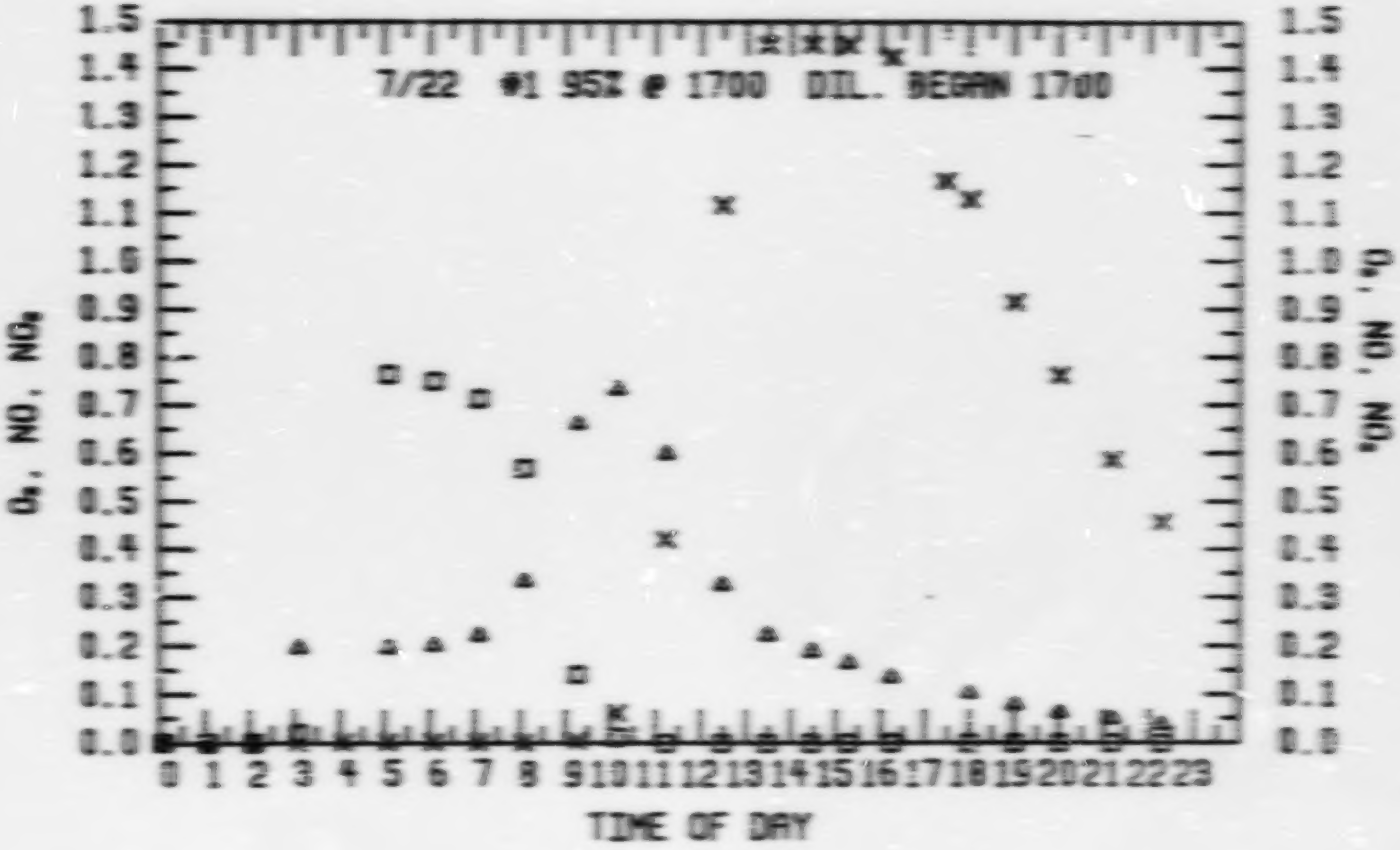
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#4 7/18
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR


7/22 #1 95% @ 1700 DIL. BEGAN 1700
O_3, NO, NO_2
O_3, NO, NO_2
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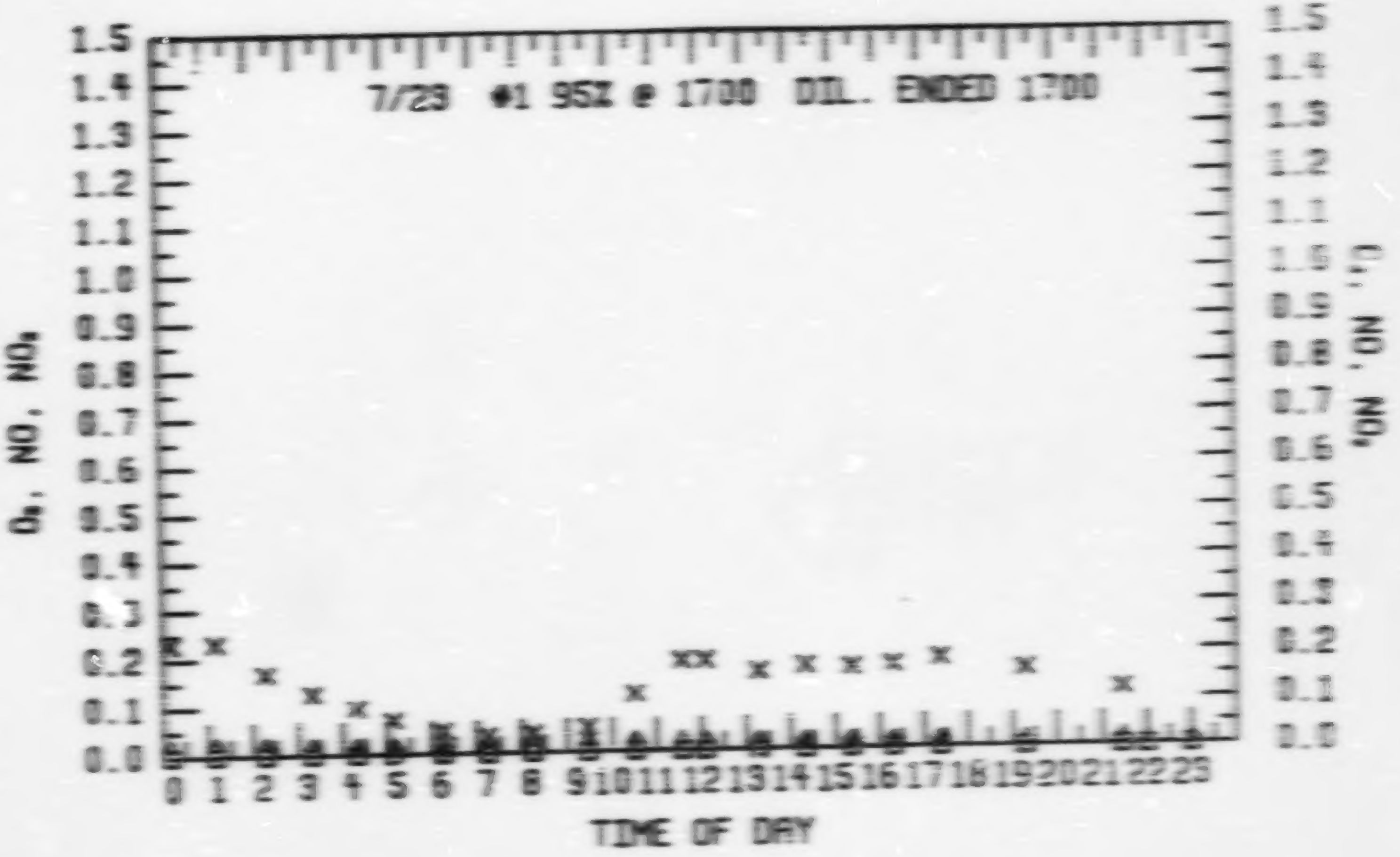
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/23 #1 95% @ 1700 DIL. ENDED 1700
O_3, NO, NO_2
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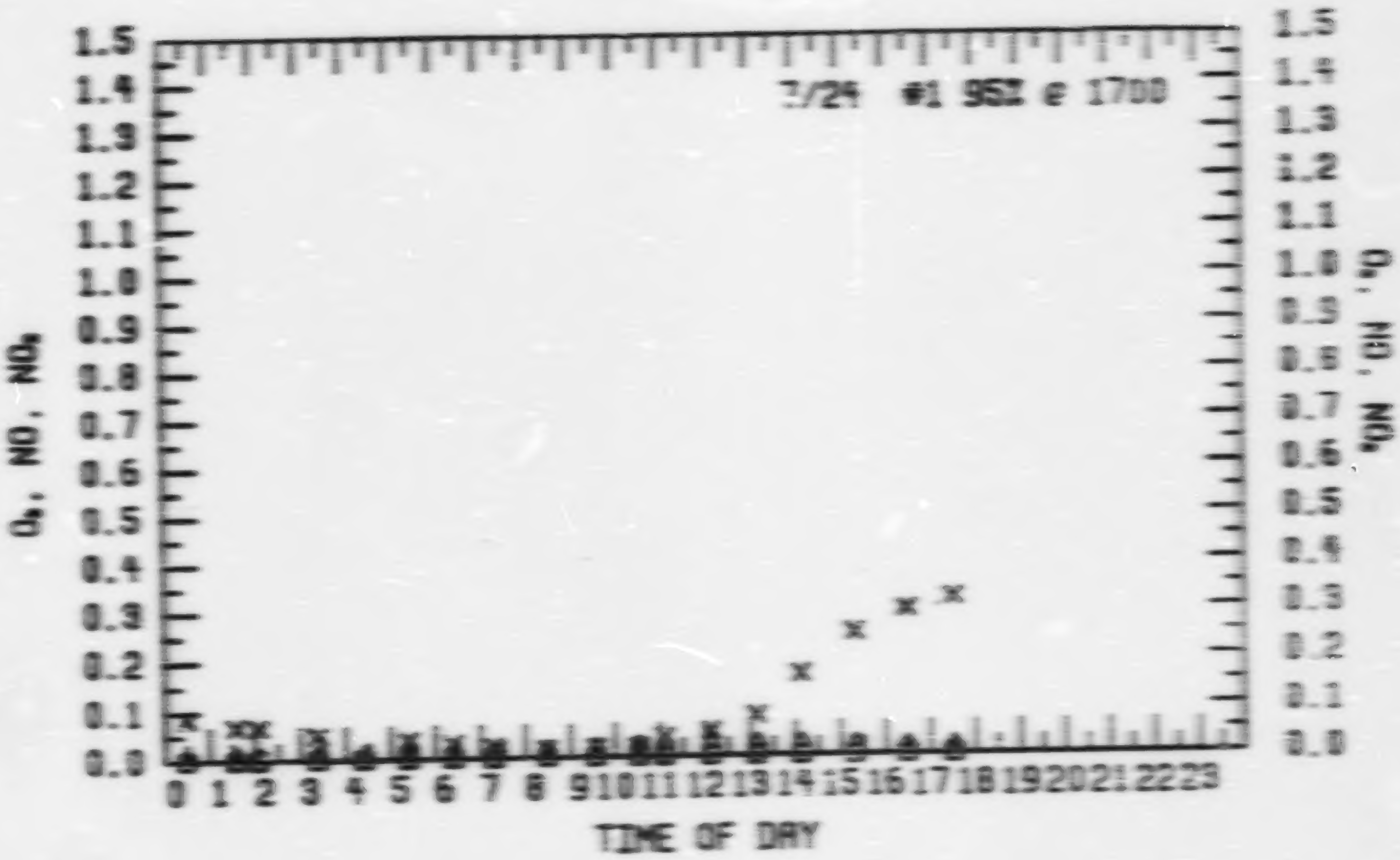
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/25 #1 95% @ 1700
O_3, NO, NO_2
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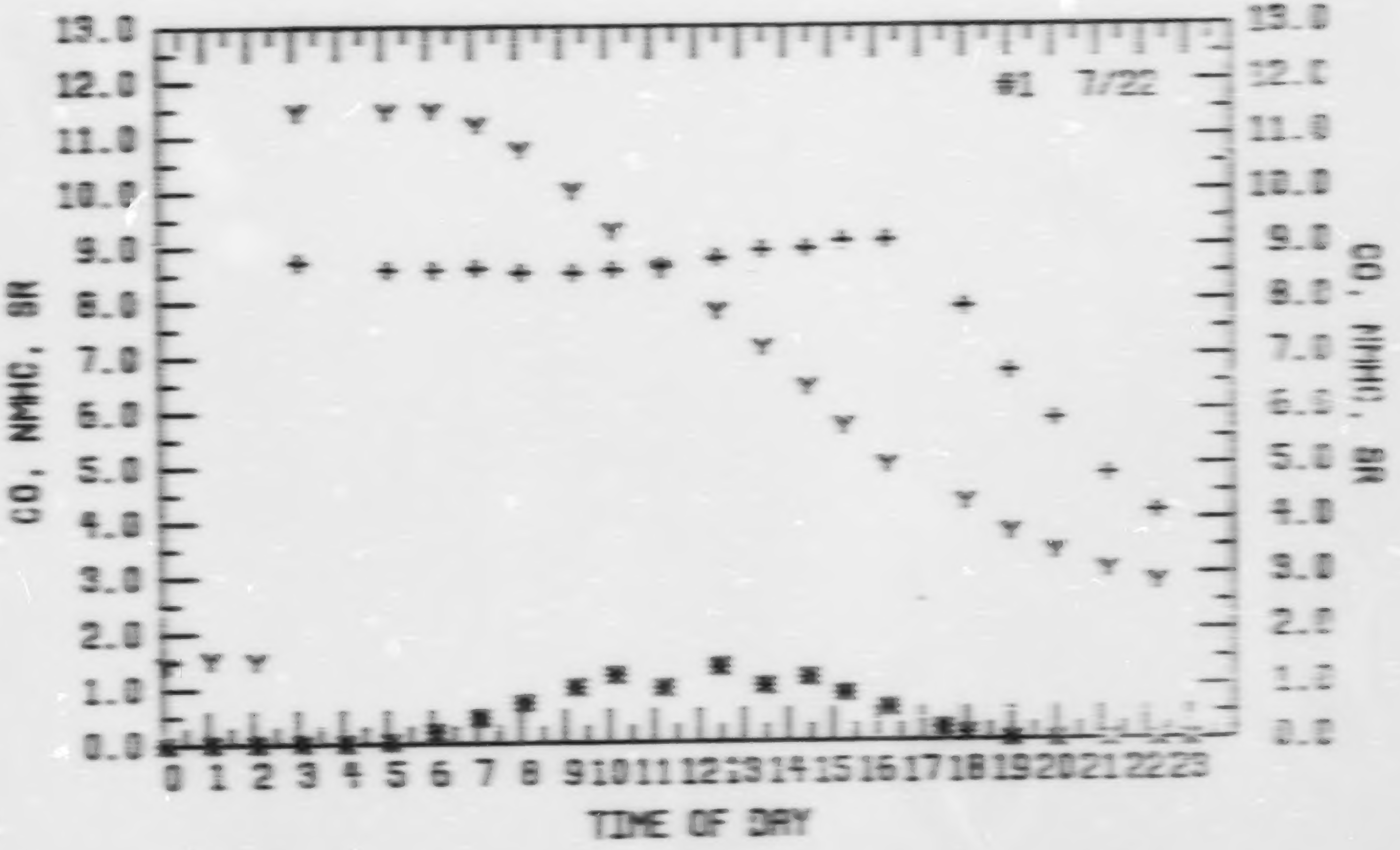
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#1 7/22
CO, NMHC, SR
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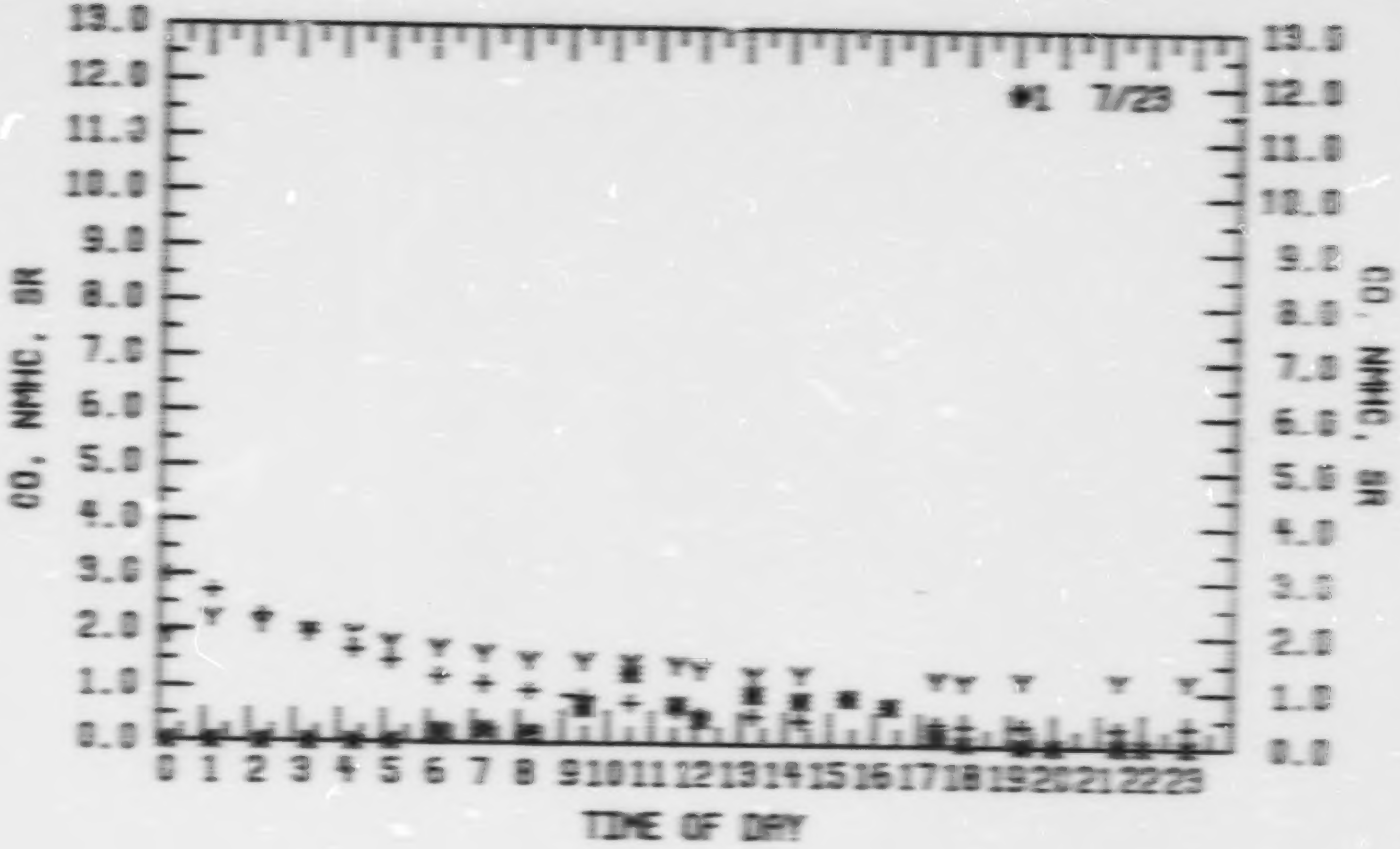
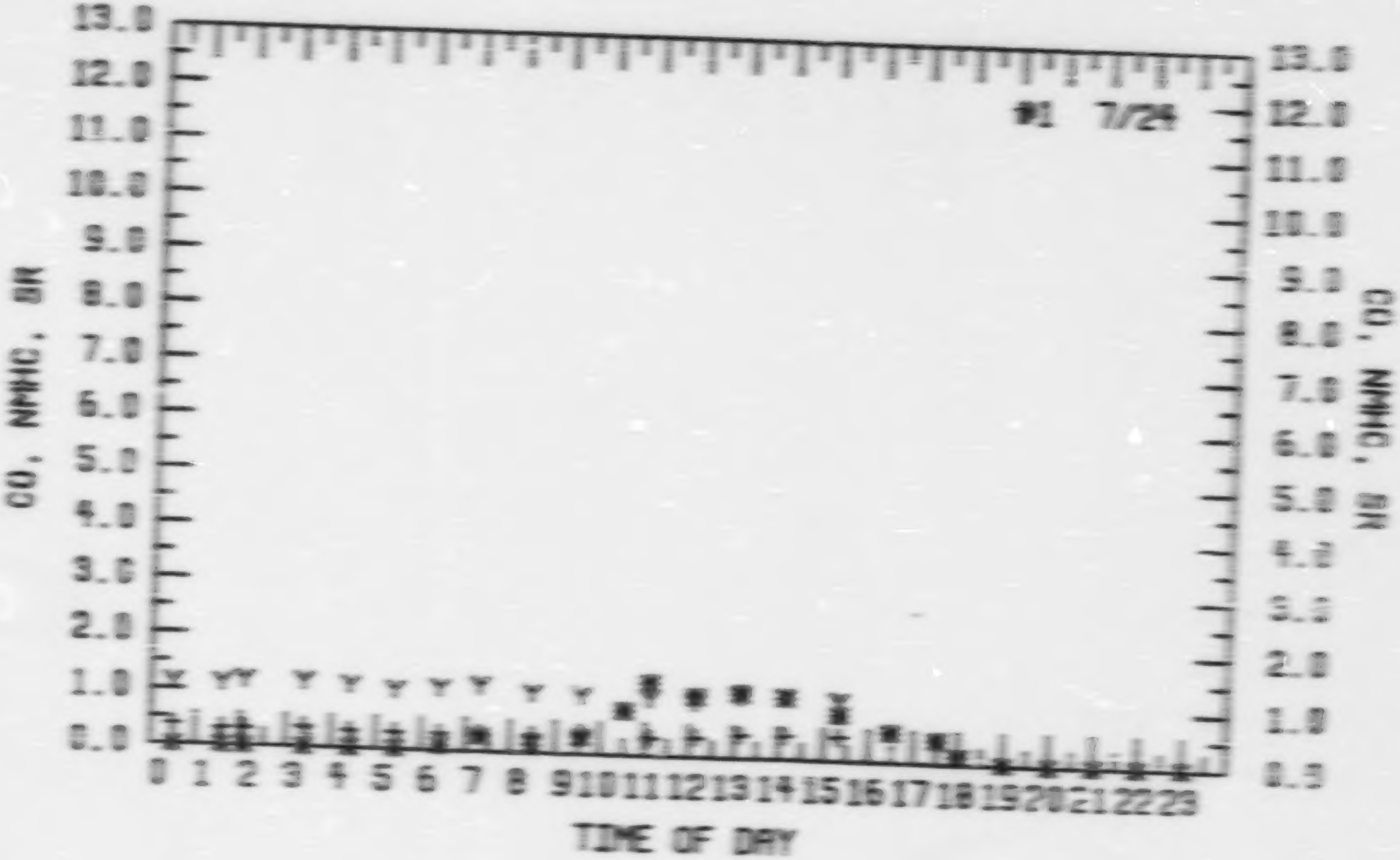
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
#1 7/23
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
13.0
12.0
11.0
10.0
9.2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR


#1 7/24
CO, NMHC, SR
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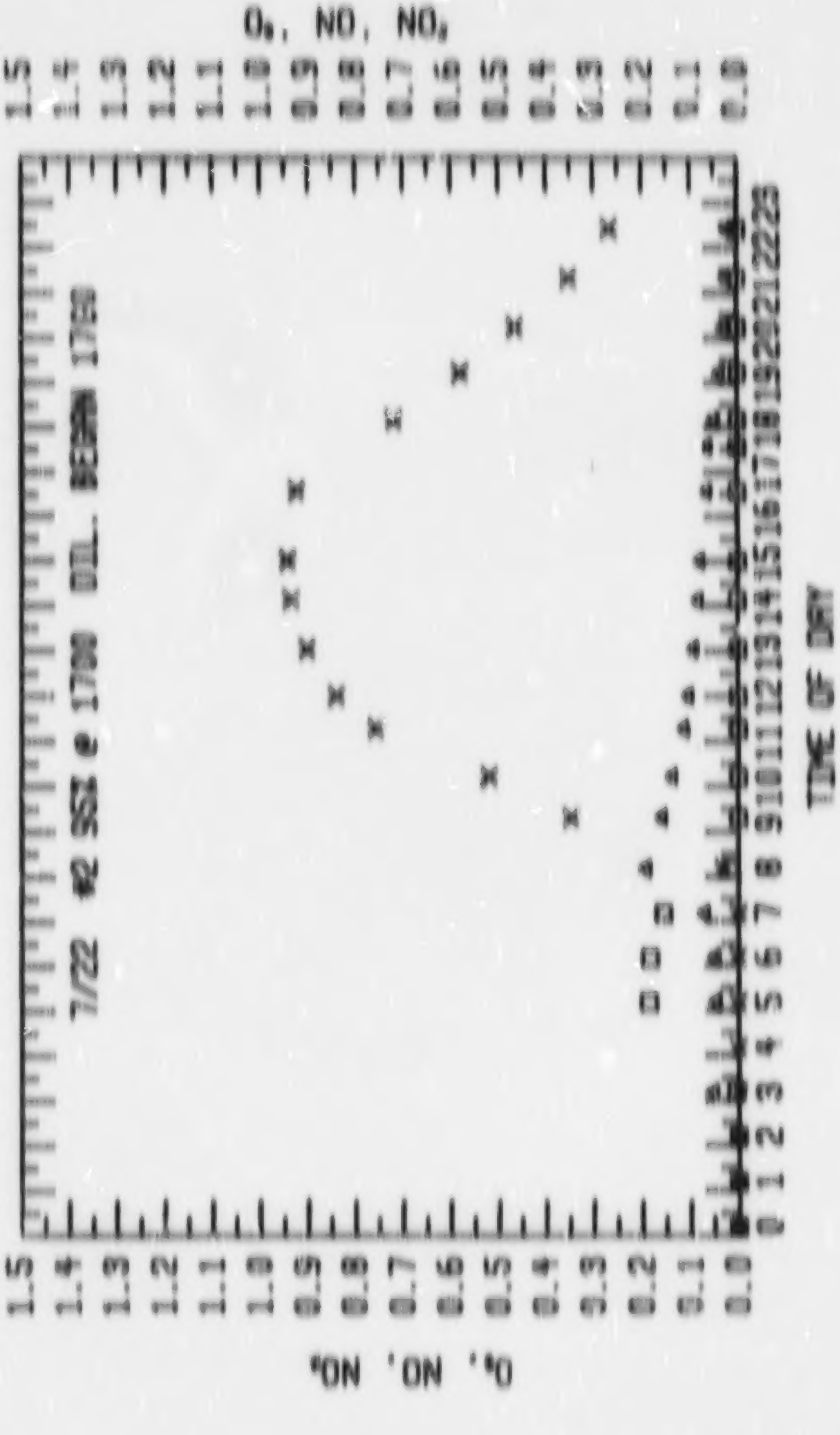
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/22 #2 SSI @ 1700 DIL. BEGAN 1750
O₃, NO, NO₂
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1.4
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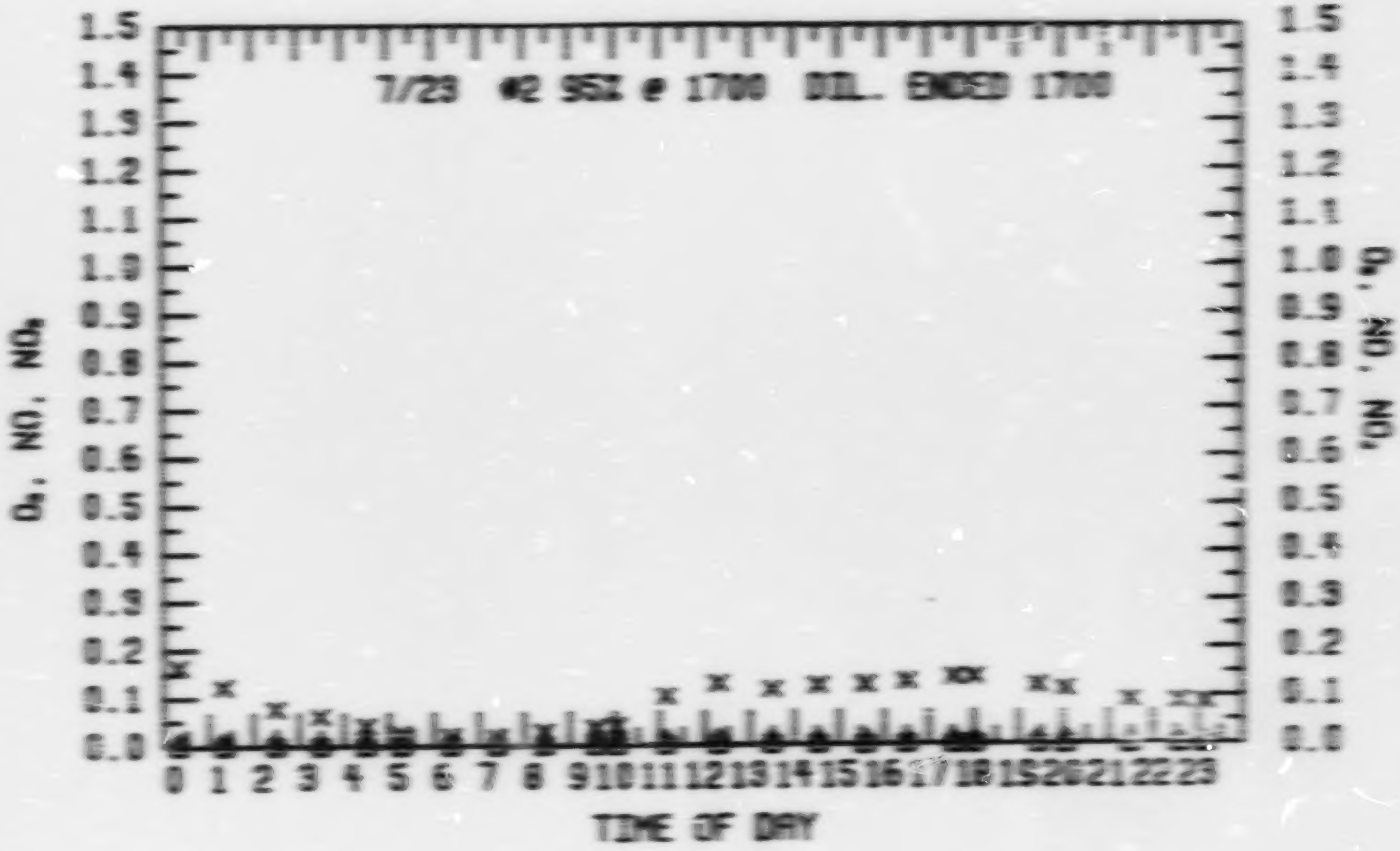
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/23 #2 95% @ 1700 DIL. ENDED 1700
O_3, NO, NO_2
O_3, NO, NO_2
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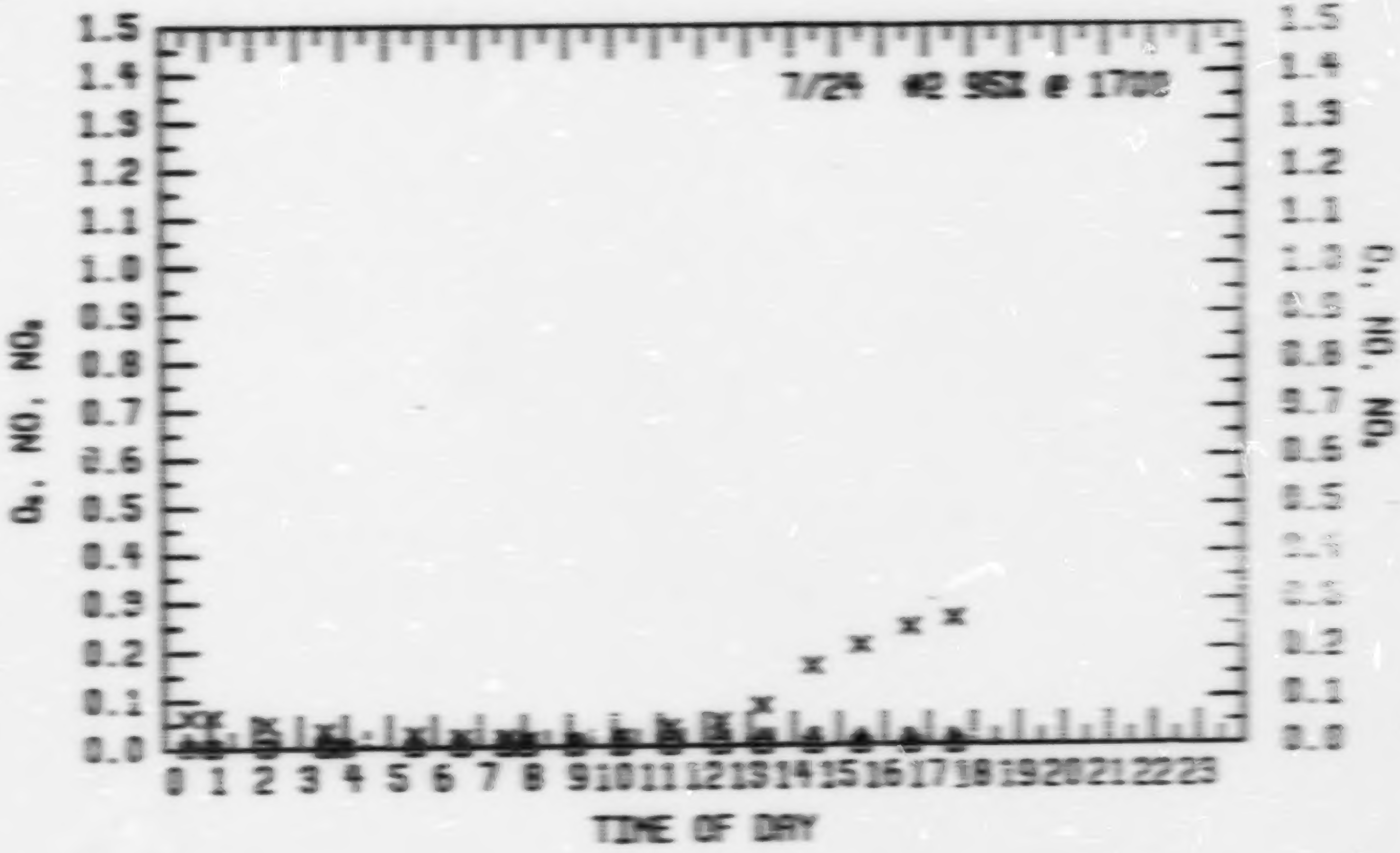
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/24 #2 95% @ 1700
O3, NO, NO2
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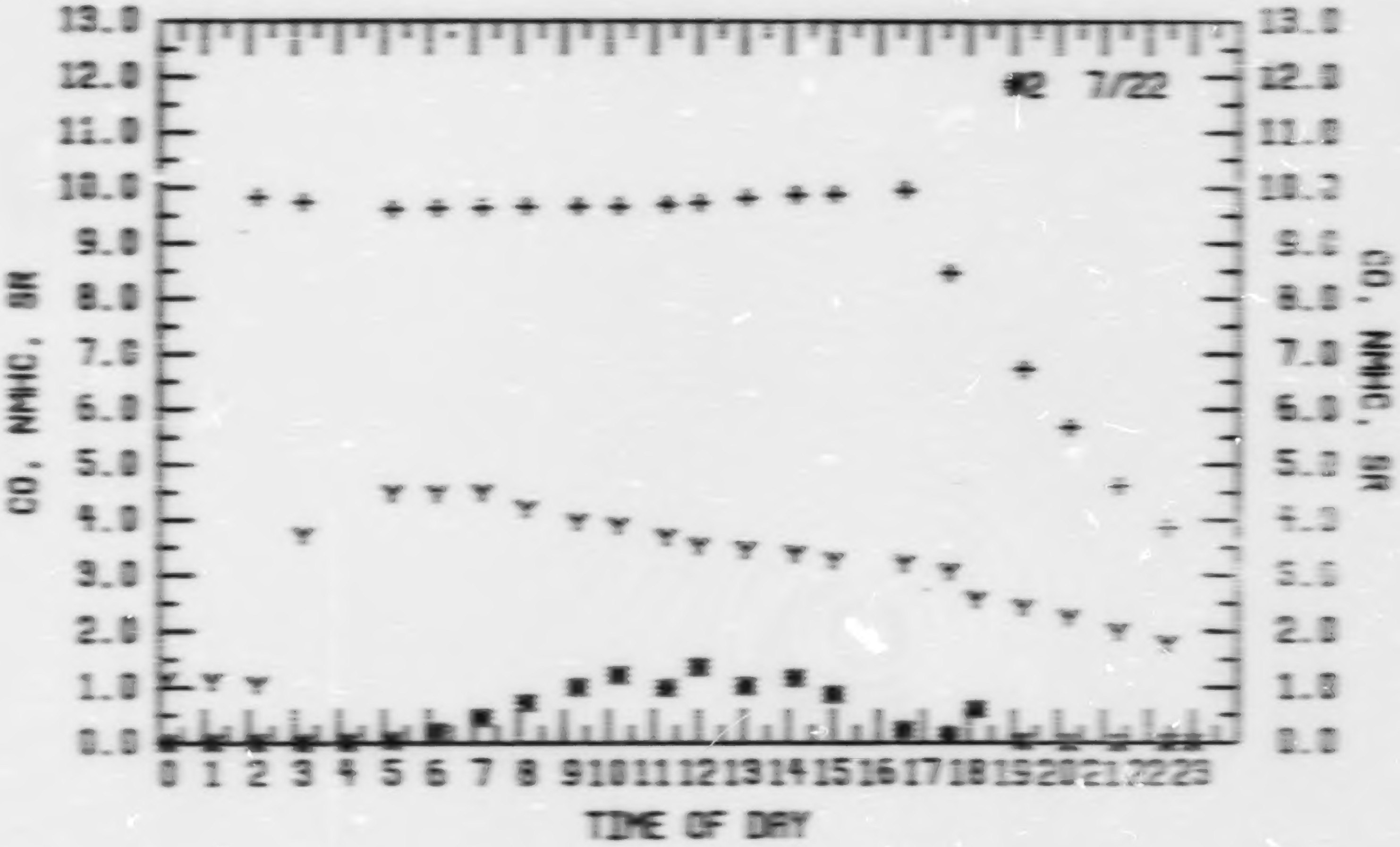
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#2 7/22
CO, NMHC, SR
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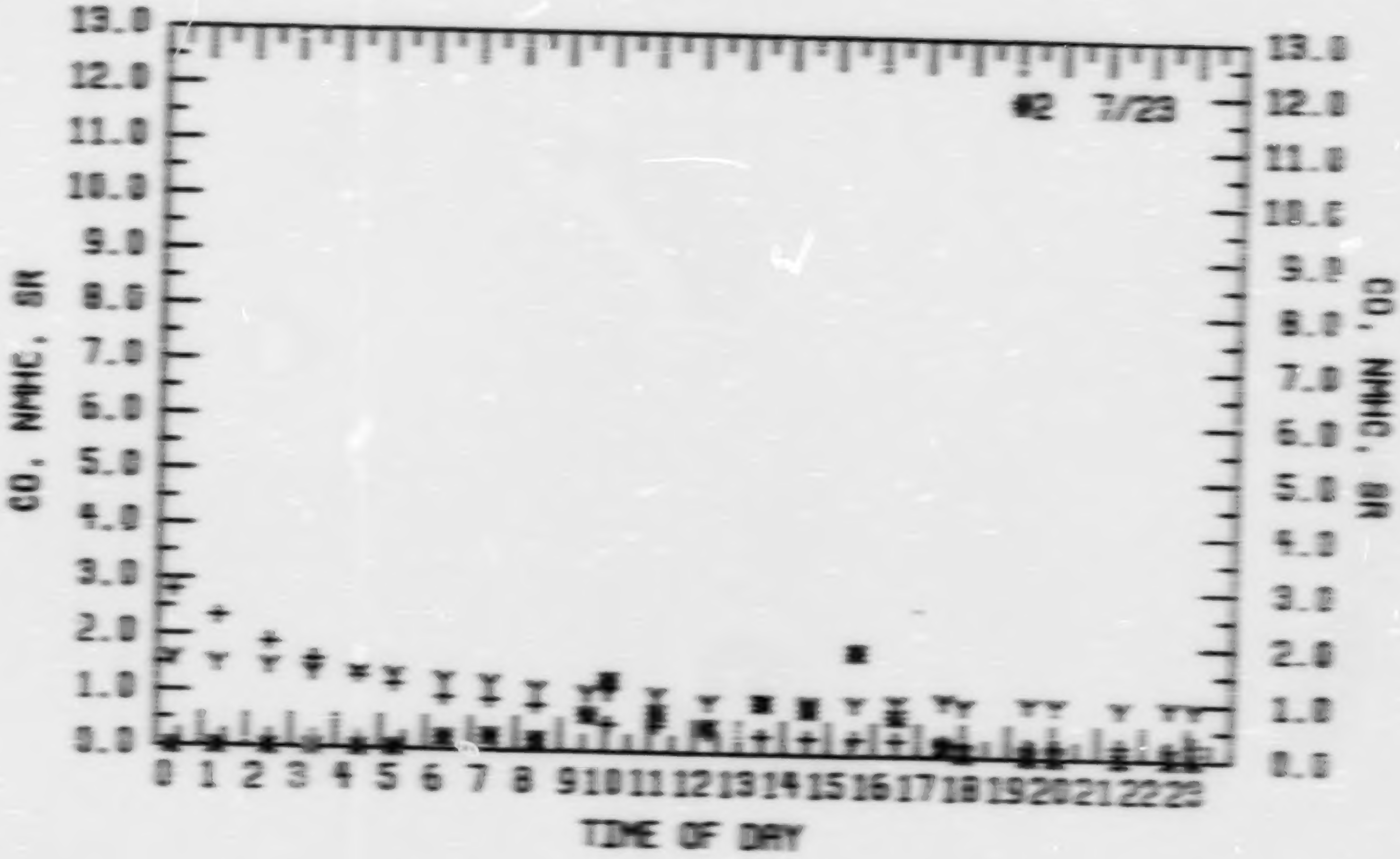
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR


#2 7/23
CO, NMHC, SR
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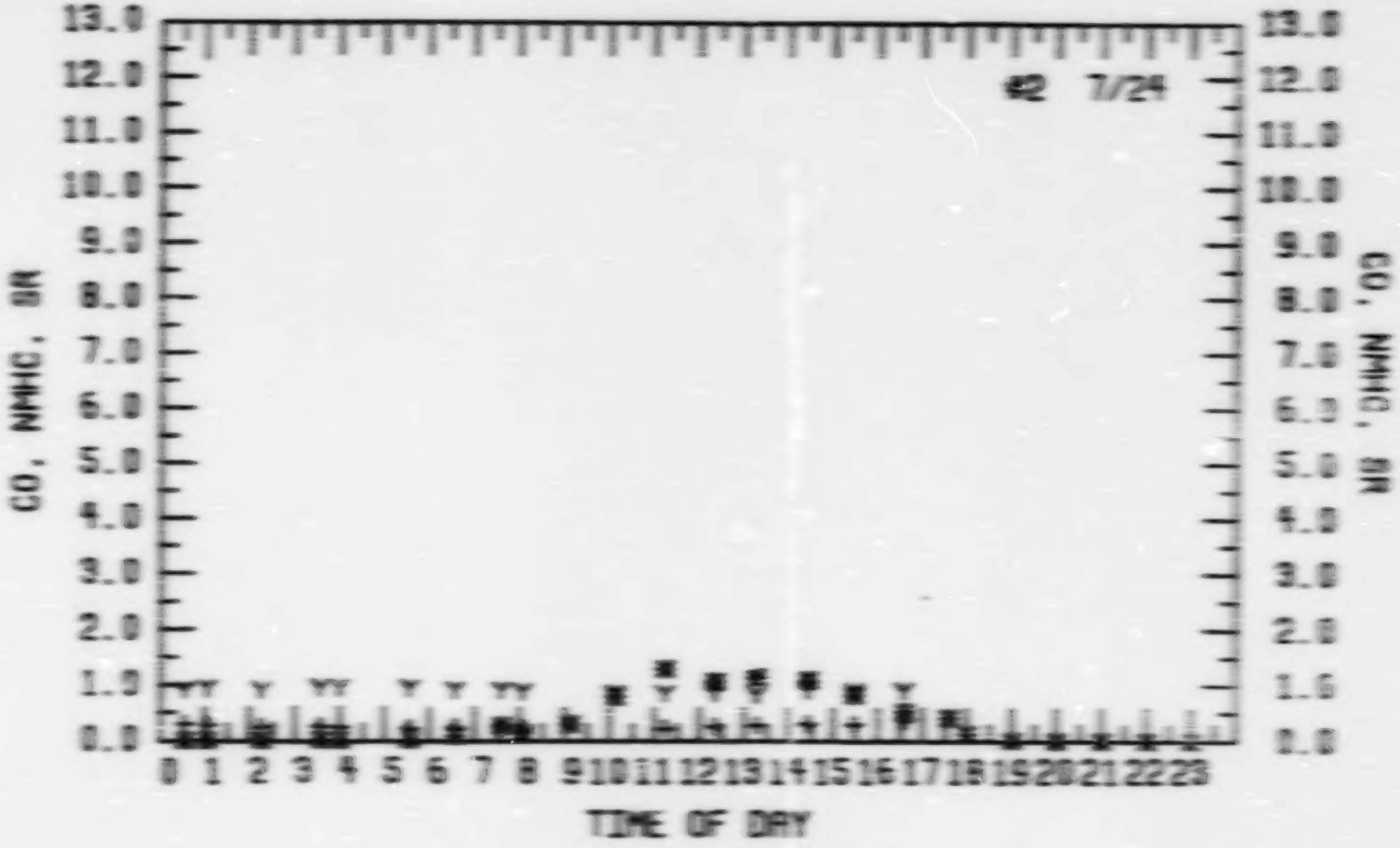
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#2 7/24
CO, NMHC, SR
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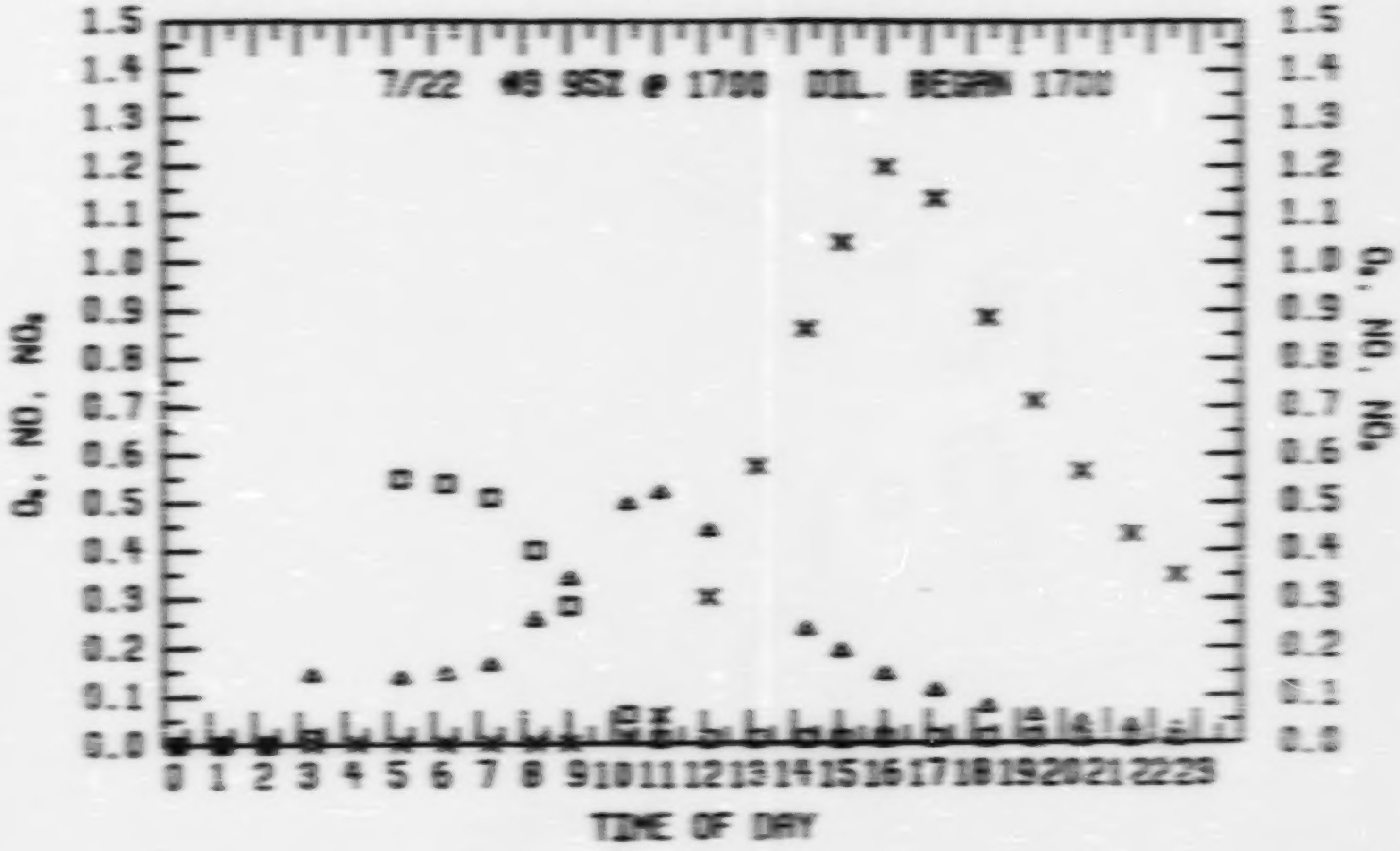
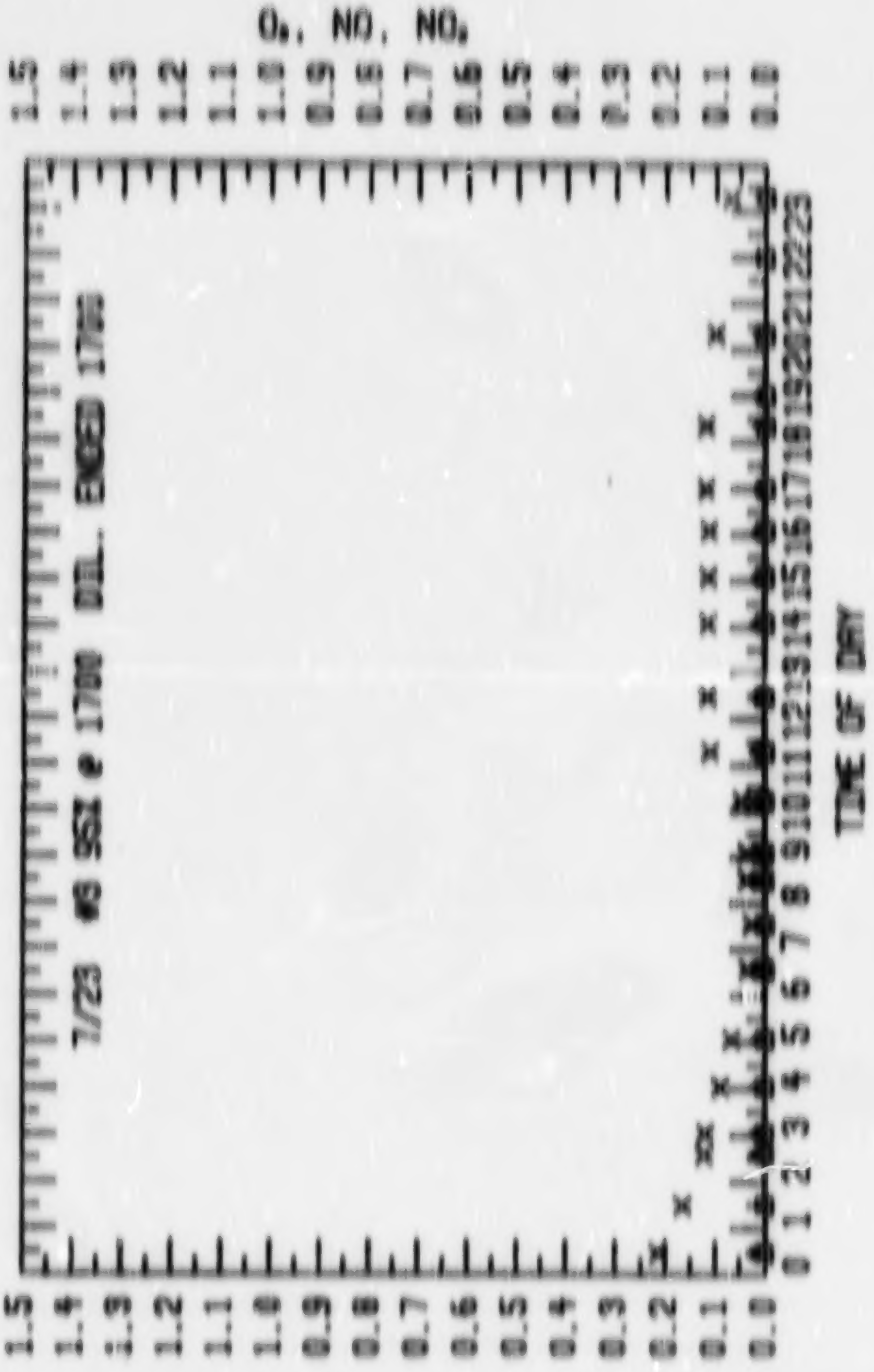
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

7/22 #3 95% @ 1700 DIL. BEGAN 1700
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/23 #3 95% @ 1700 DIL. EXCEED 1700
O₃, NO, NO₂
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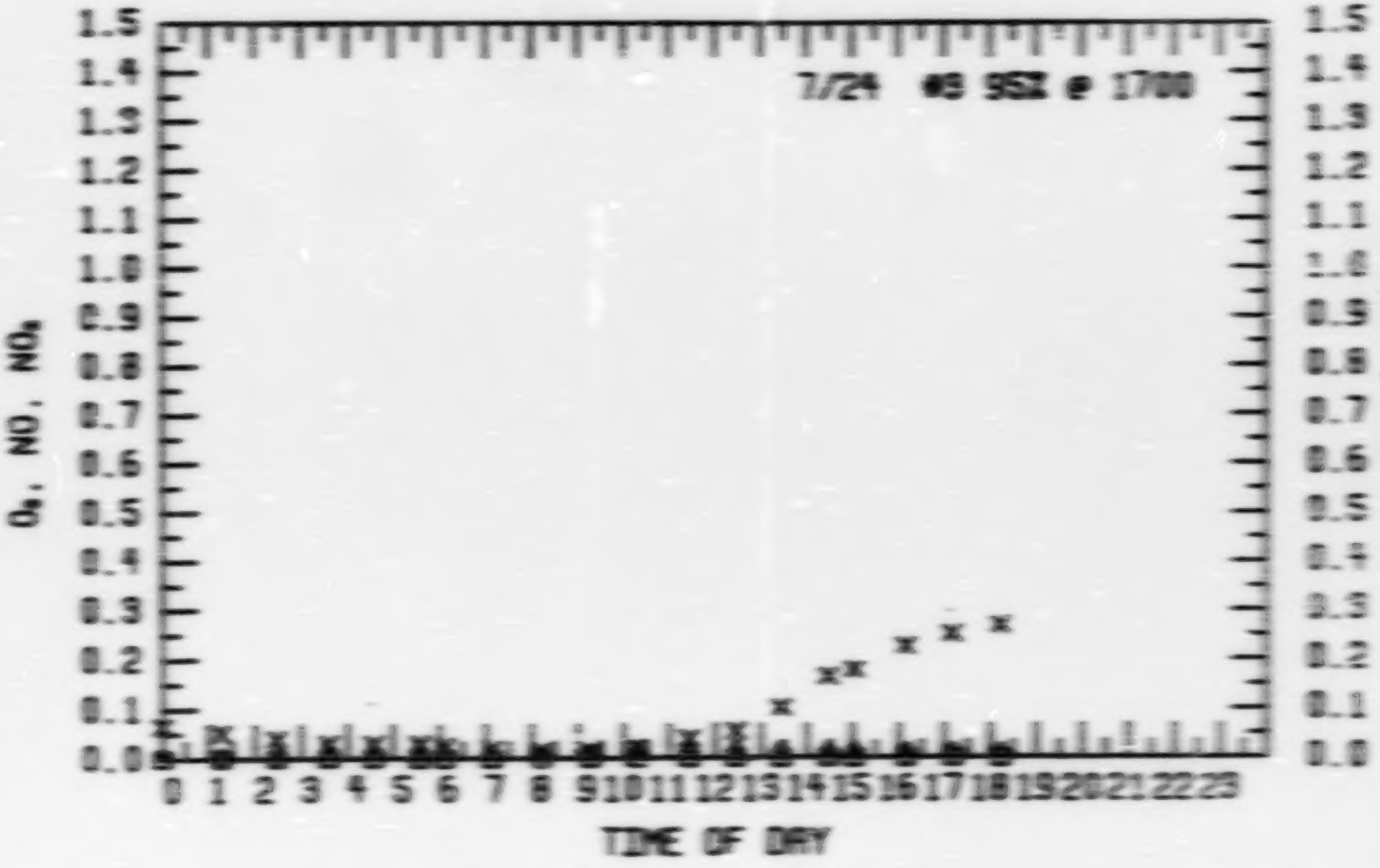
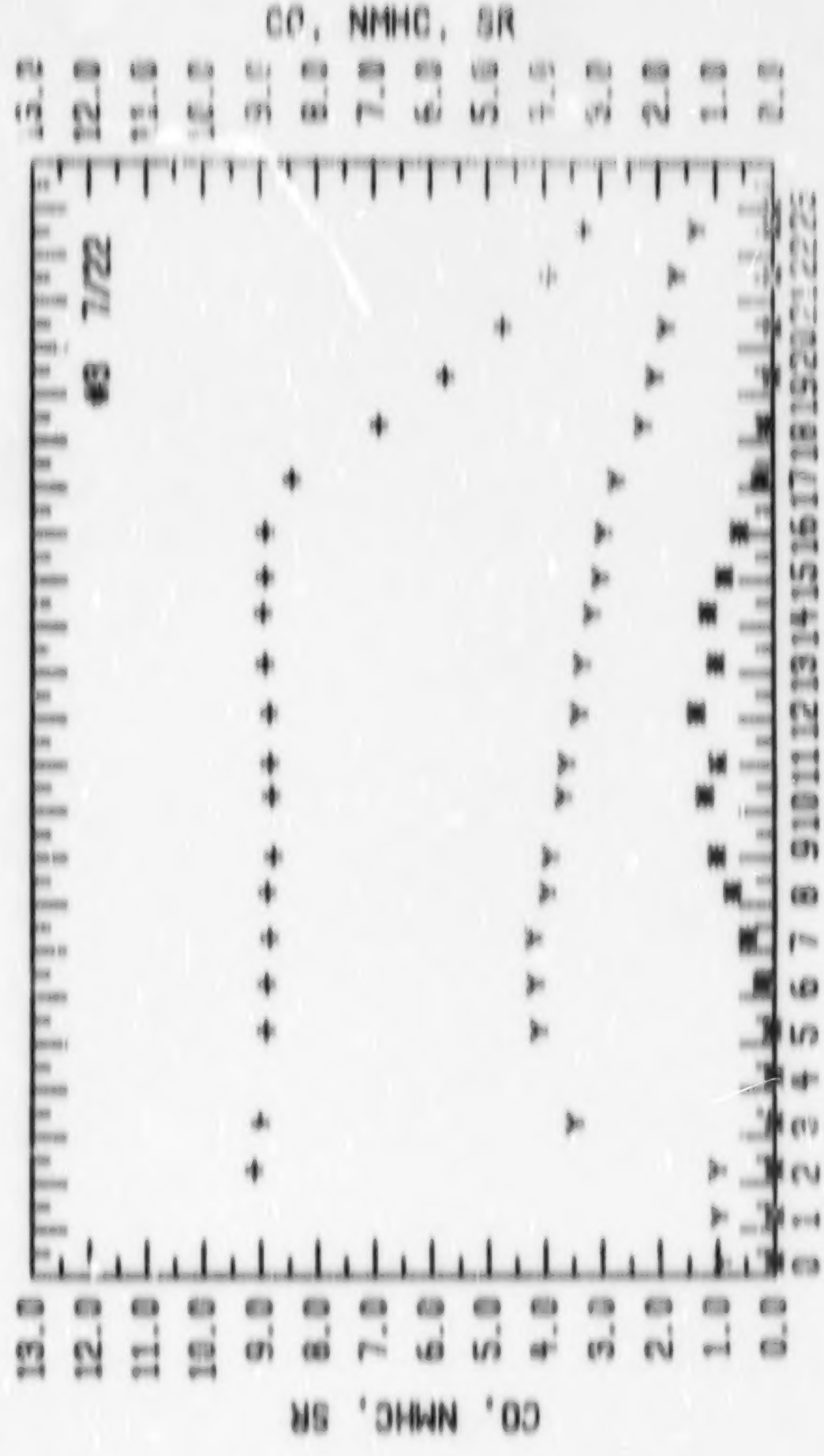
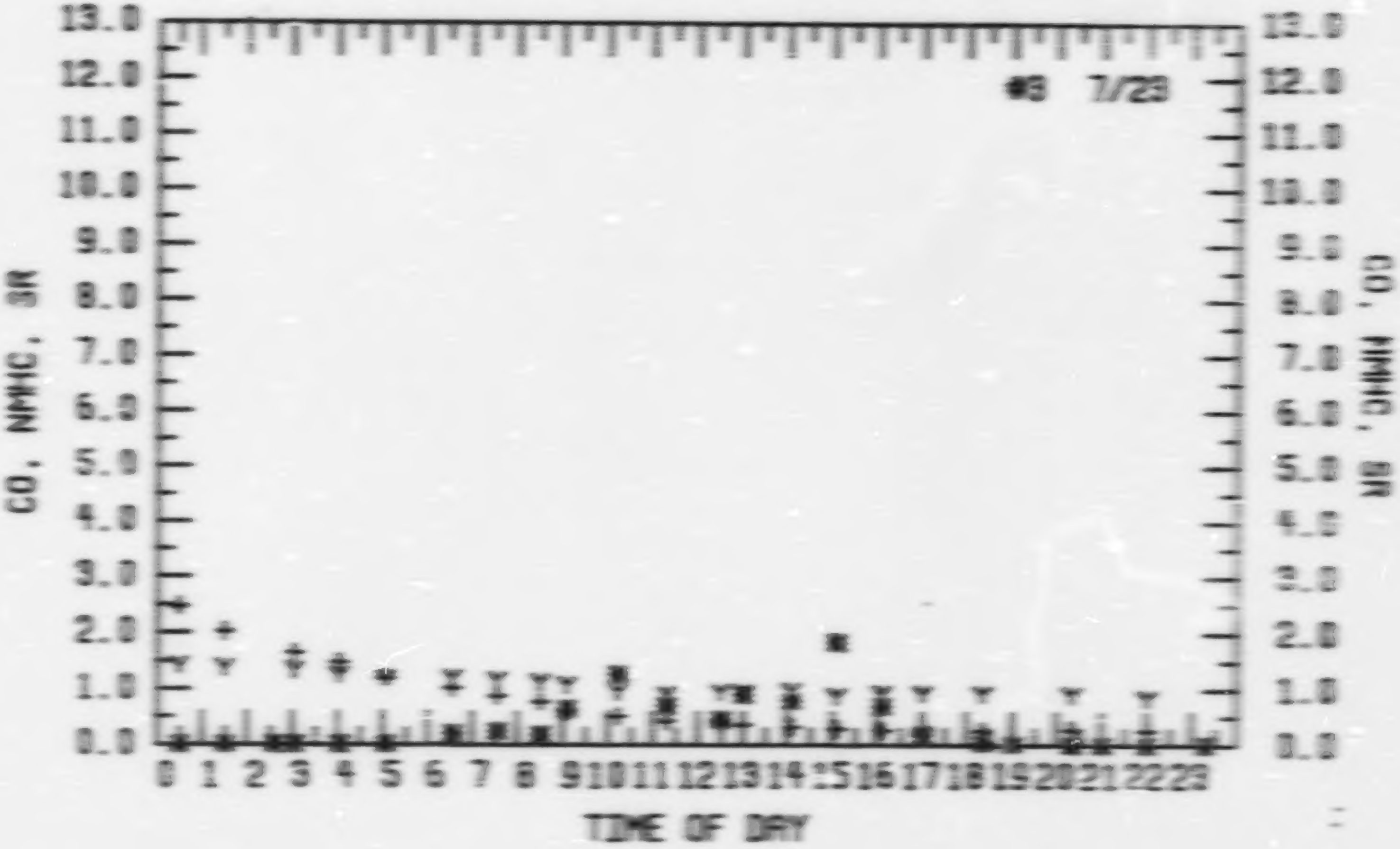
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23


7/24 #3 95% @ 1700
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY



#3 7/22
CO, NMHC, SR
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#8 7/23
CO, NMHC, SR
CO, NMHC, SR
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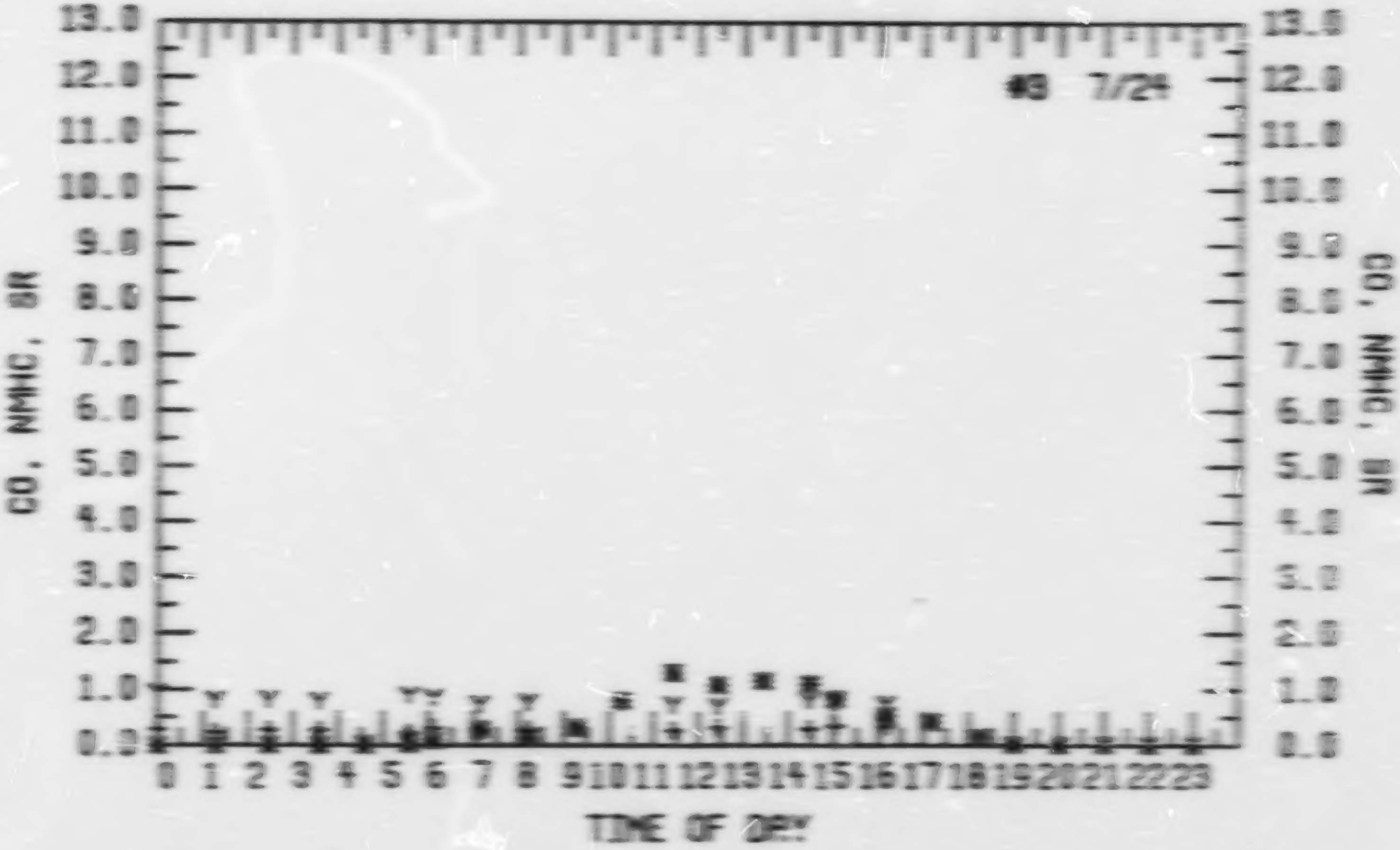
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#3 7/24
CO, NMHC, SR
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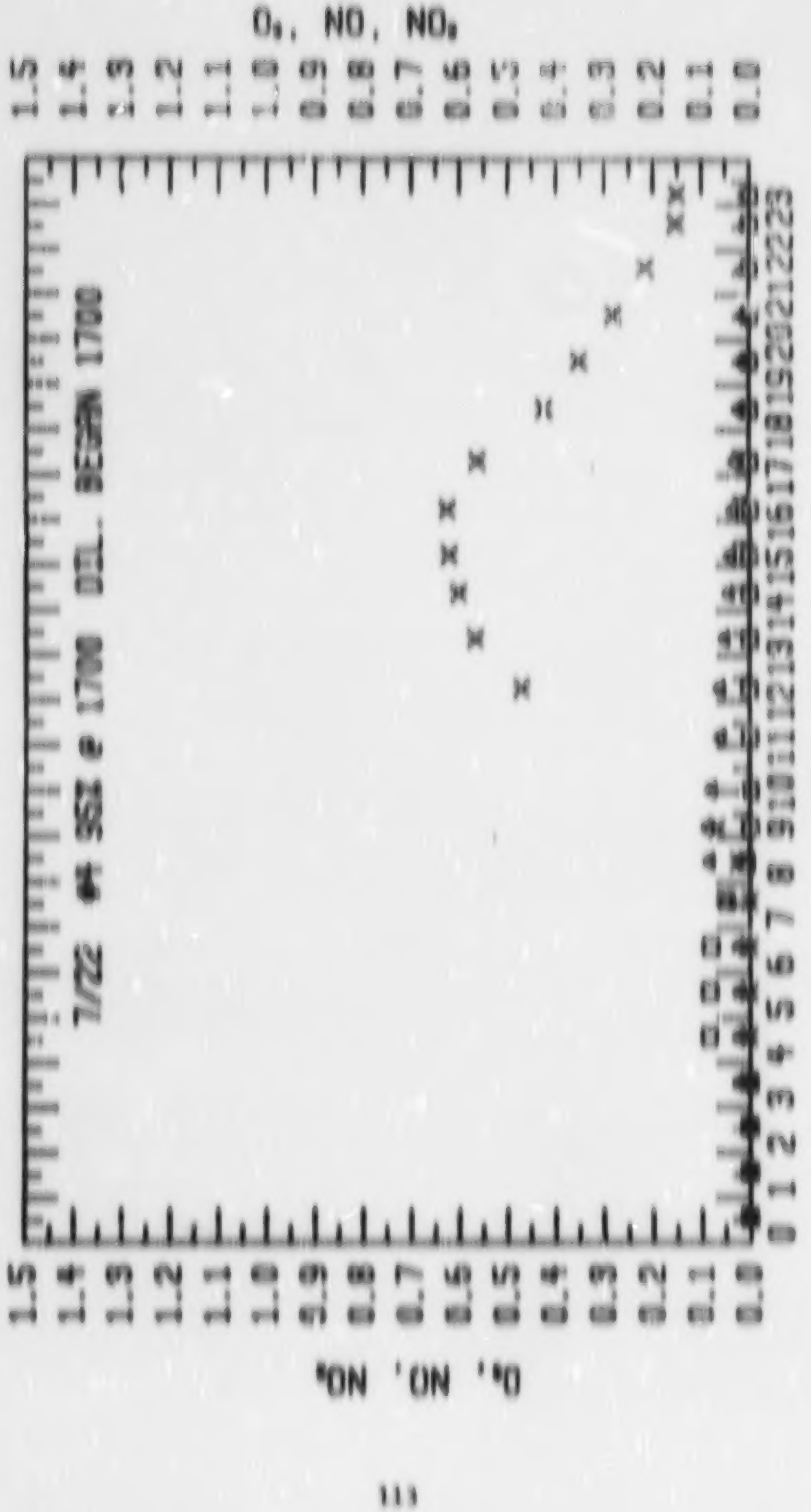
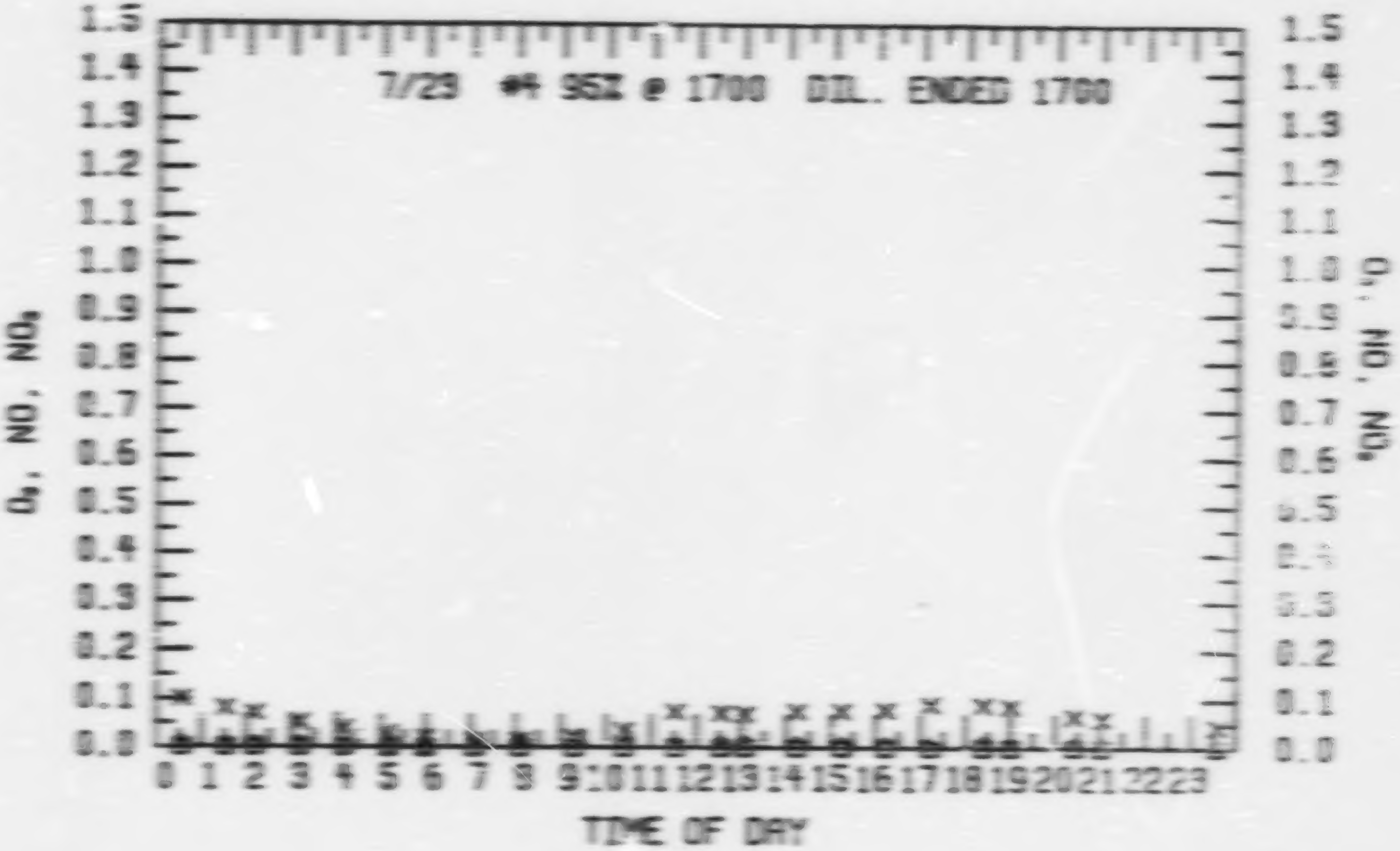
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/22 #4 SCE @ 1700 DIL. BEGAN 1700
O3, NO, NO2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


7/23 #4 95% @ 1700 DIL. ENDED 1700
O_3, NO, NO_2
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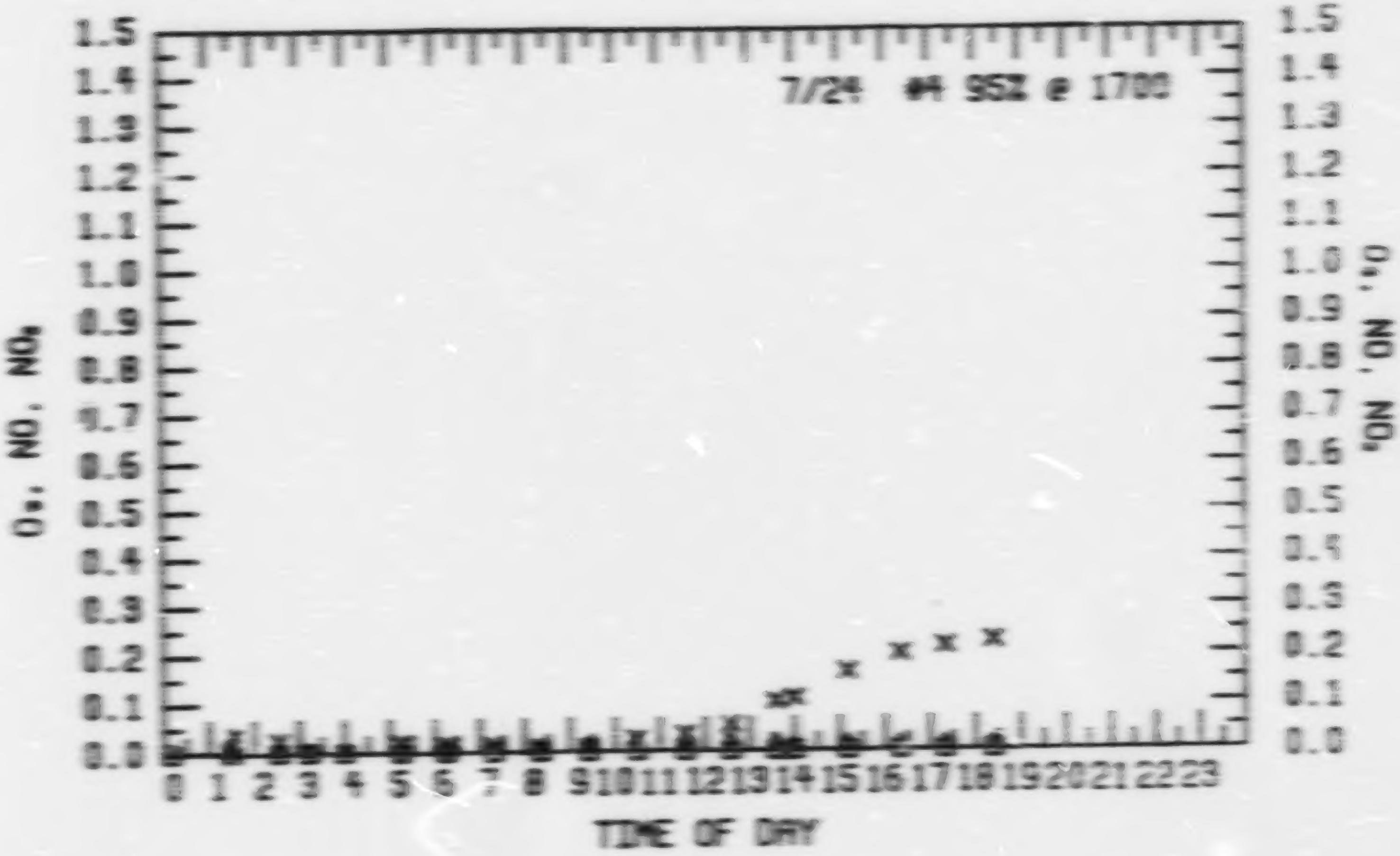
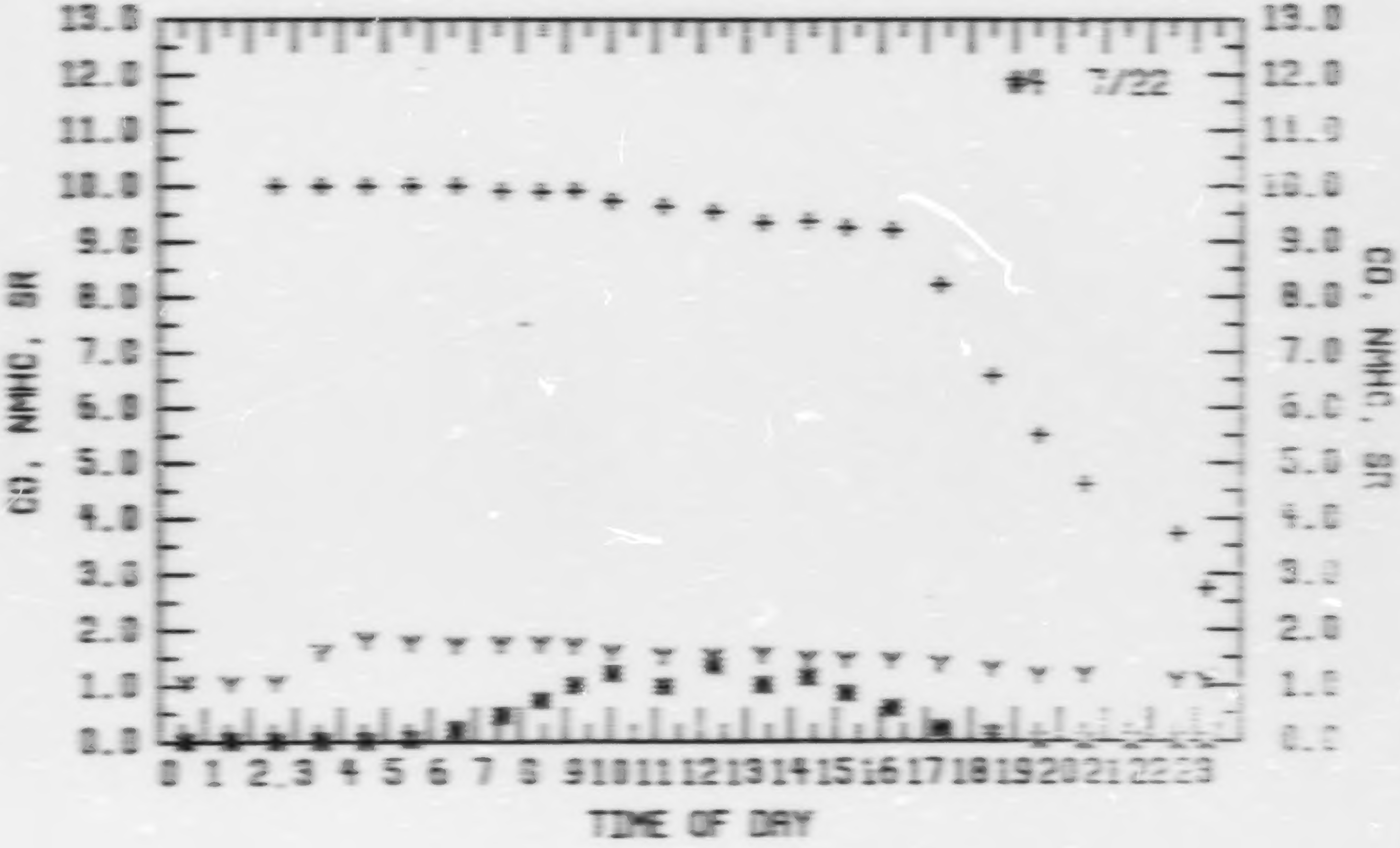
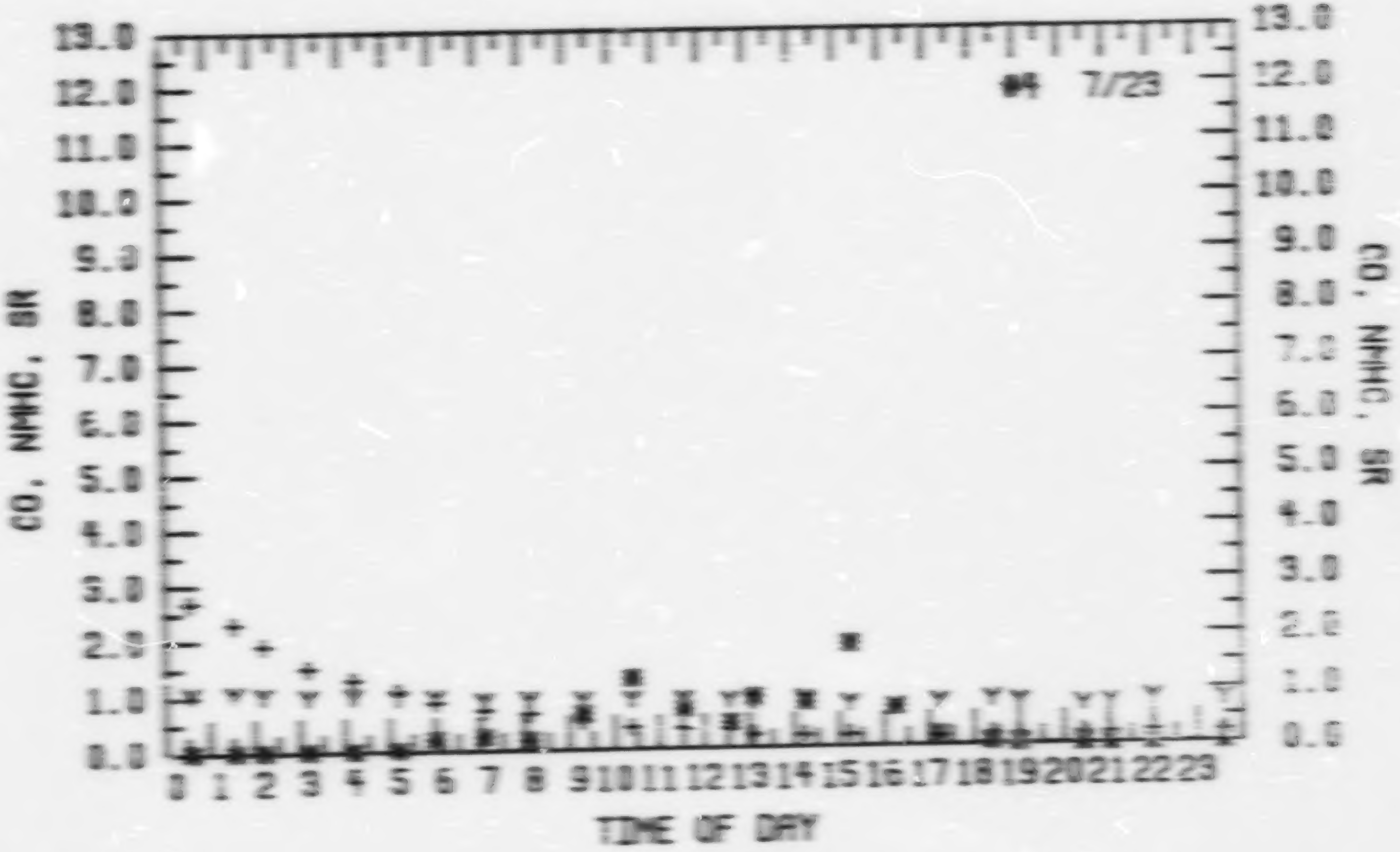
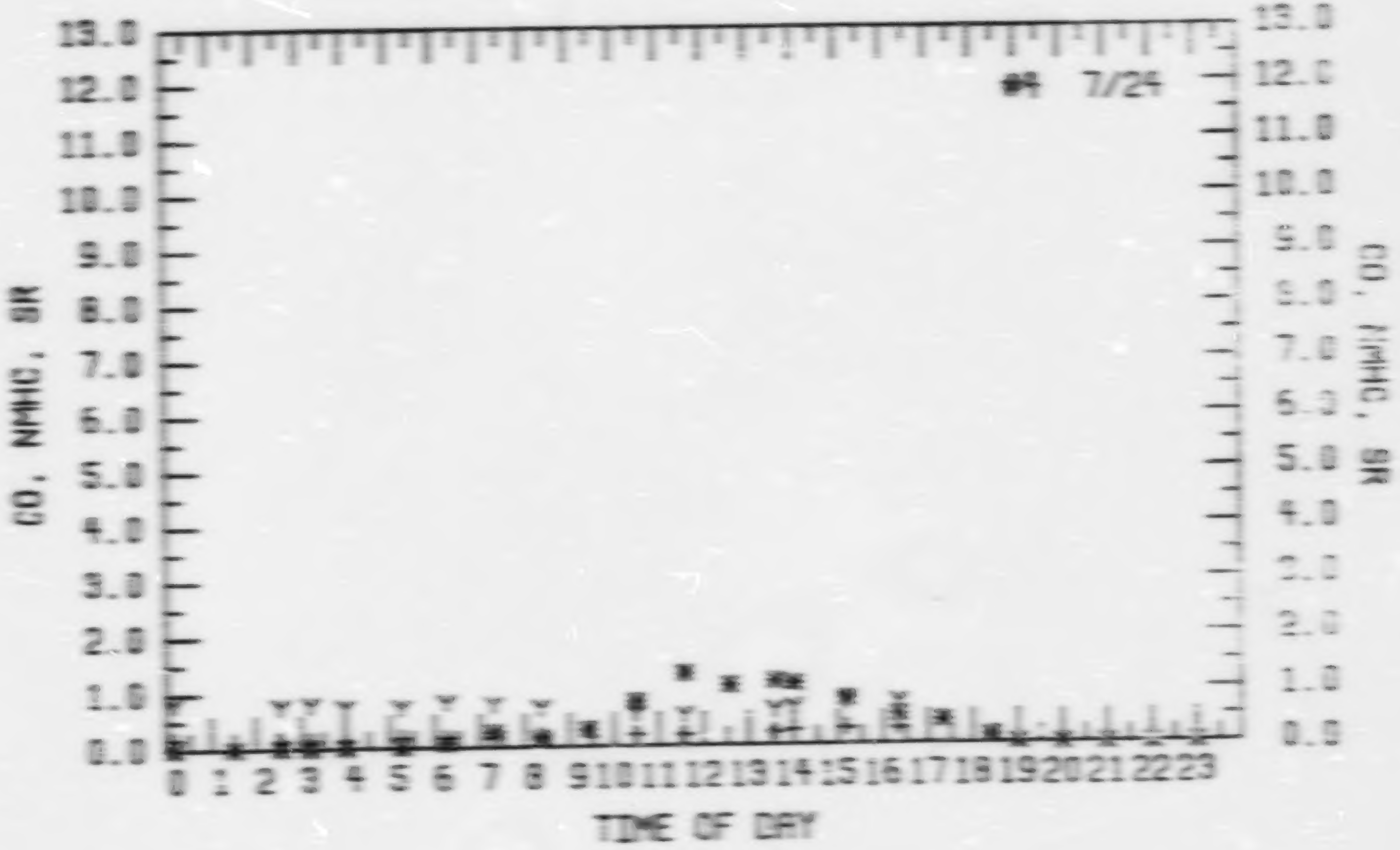
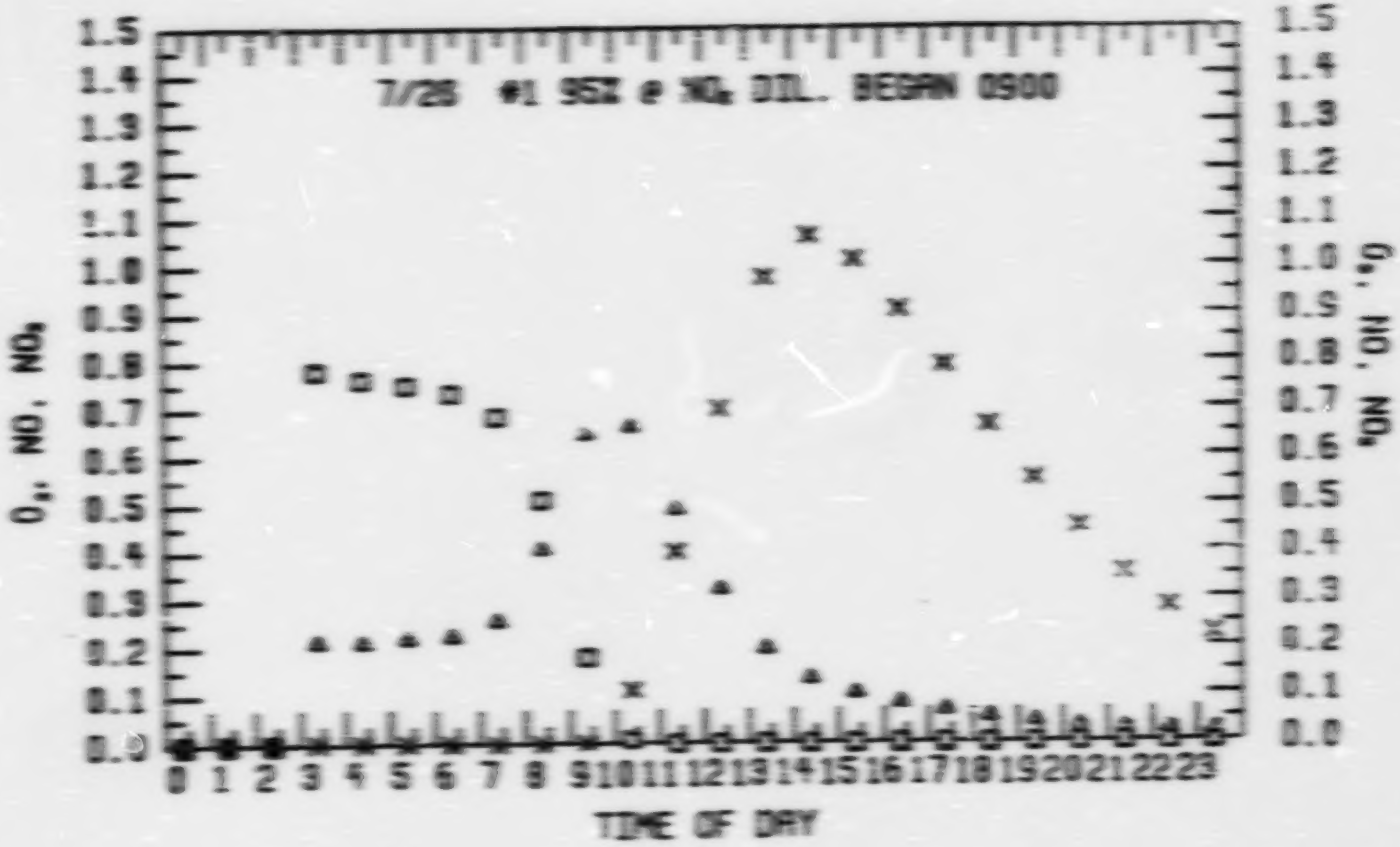
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

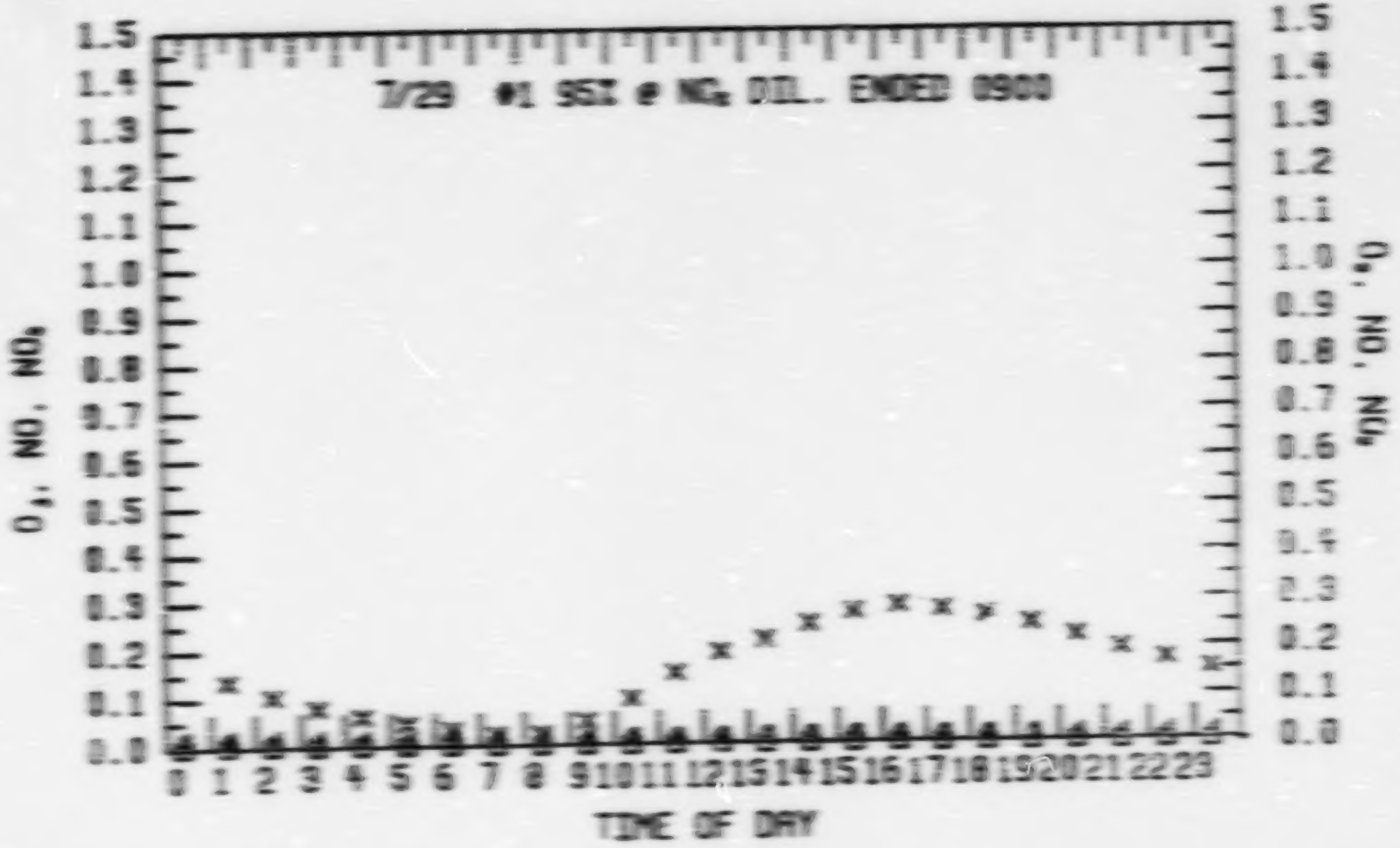

7/24 #4 95% @ 1700
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

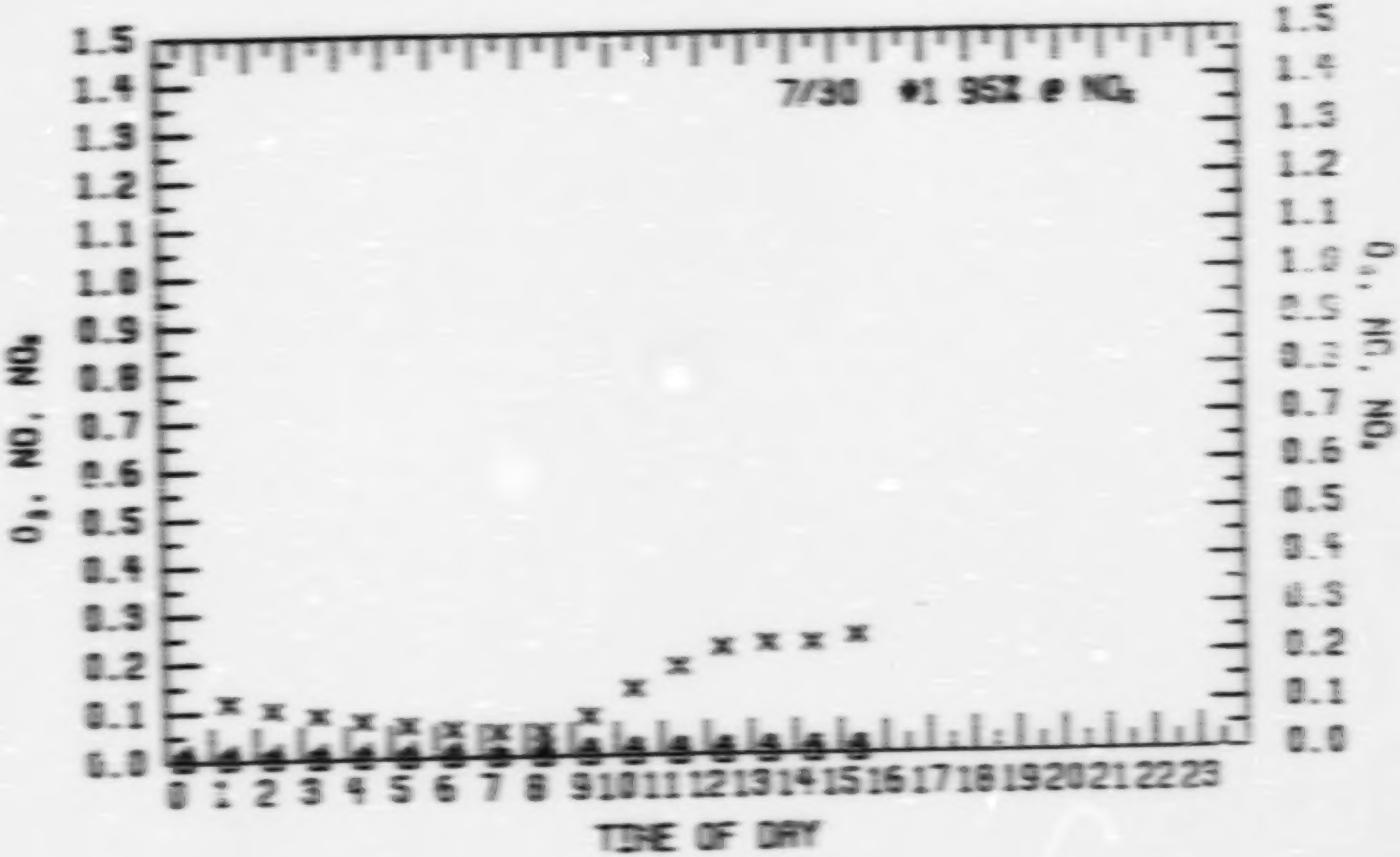

13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
#4 7/22
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

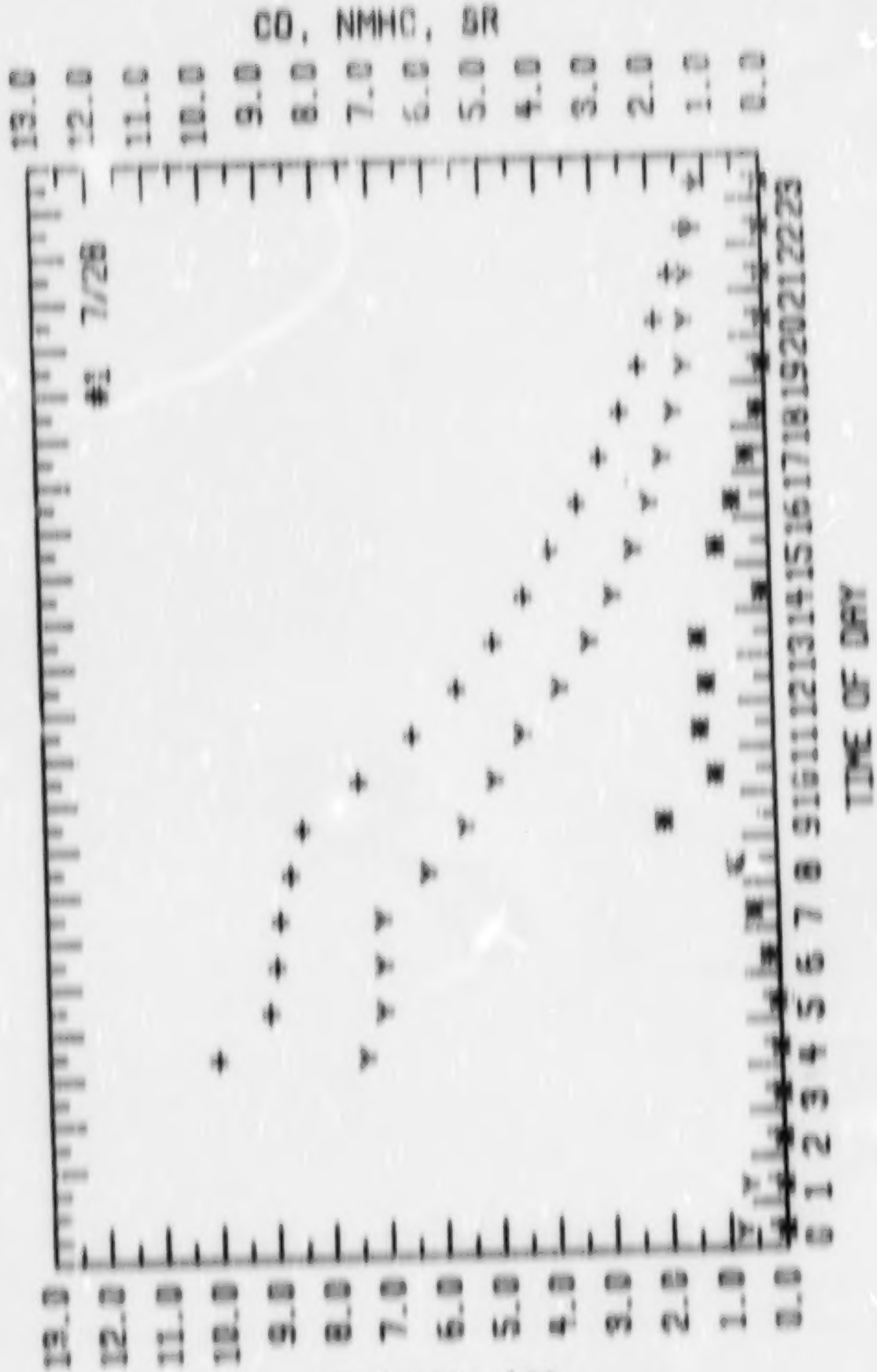

#4 7/23
CO, NMHC, SR
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#4 7/24
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

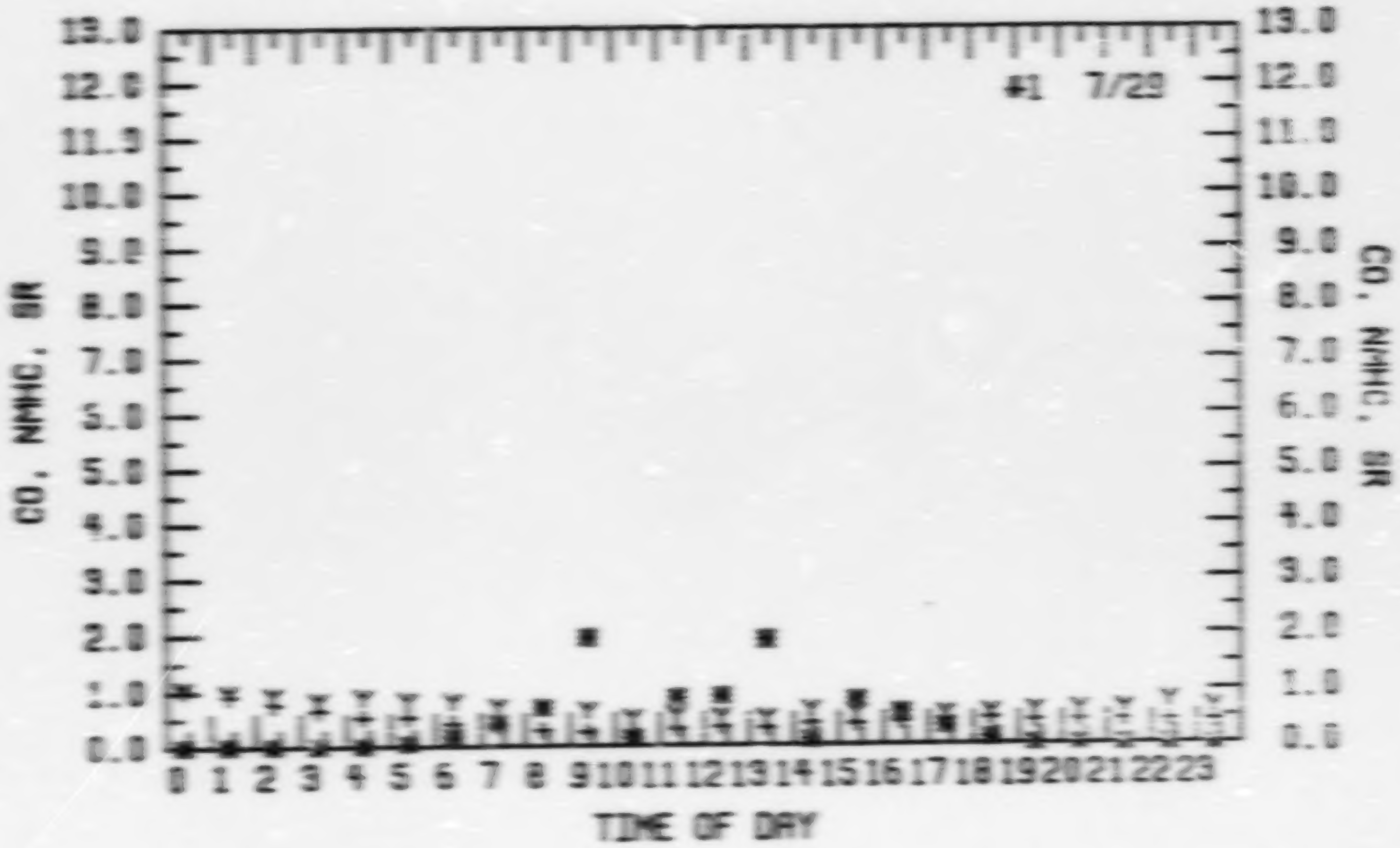

7/26 #1 95% @ NO₂ DIL. BEGAN 0900
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

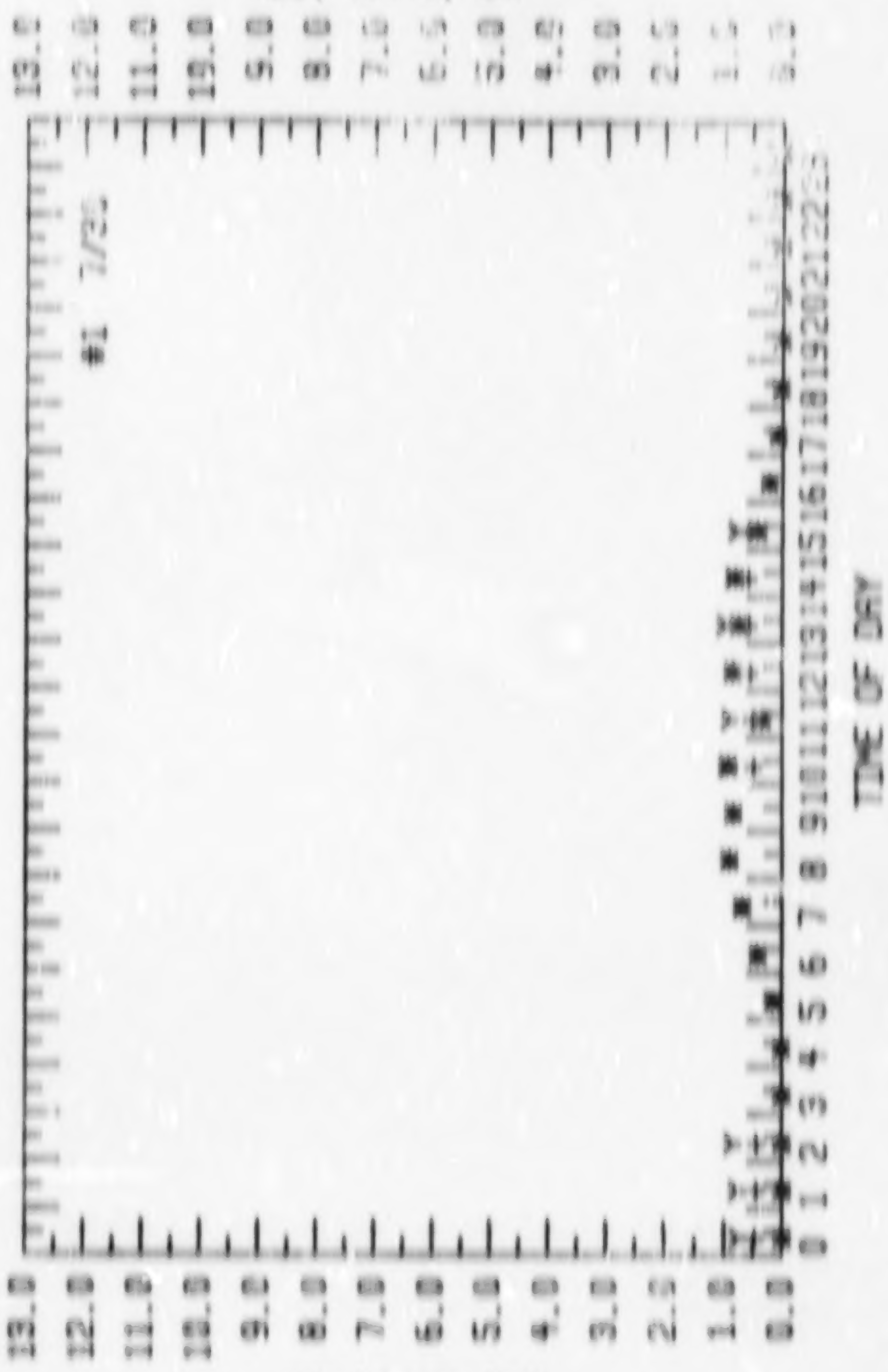

7/29 #1 95% @ NO₂ DIL. ENDED 0900
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

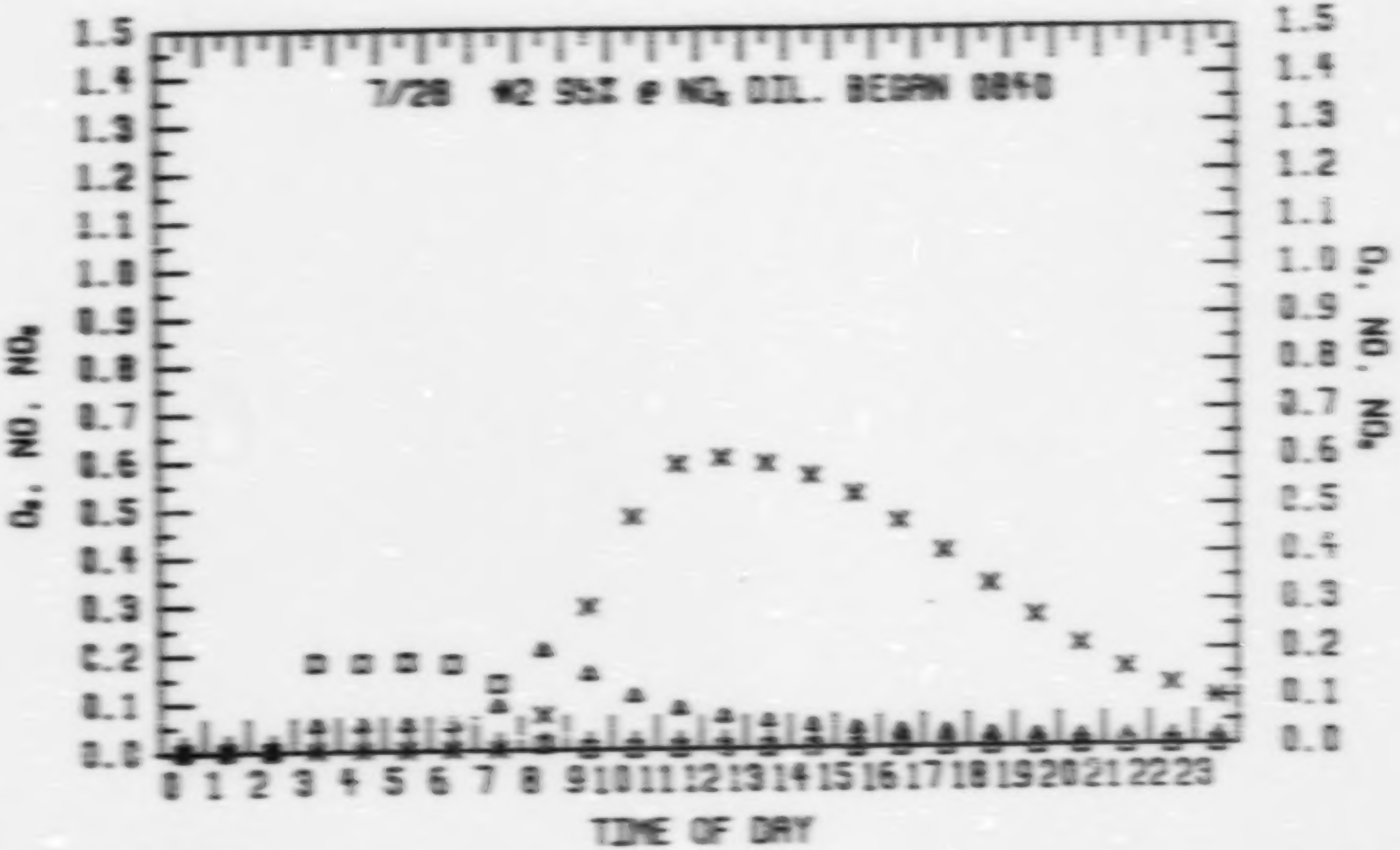

7/30 #1 95% @ NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

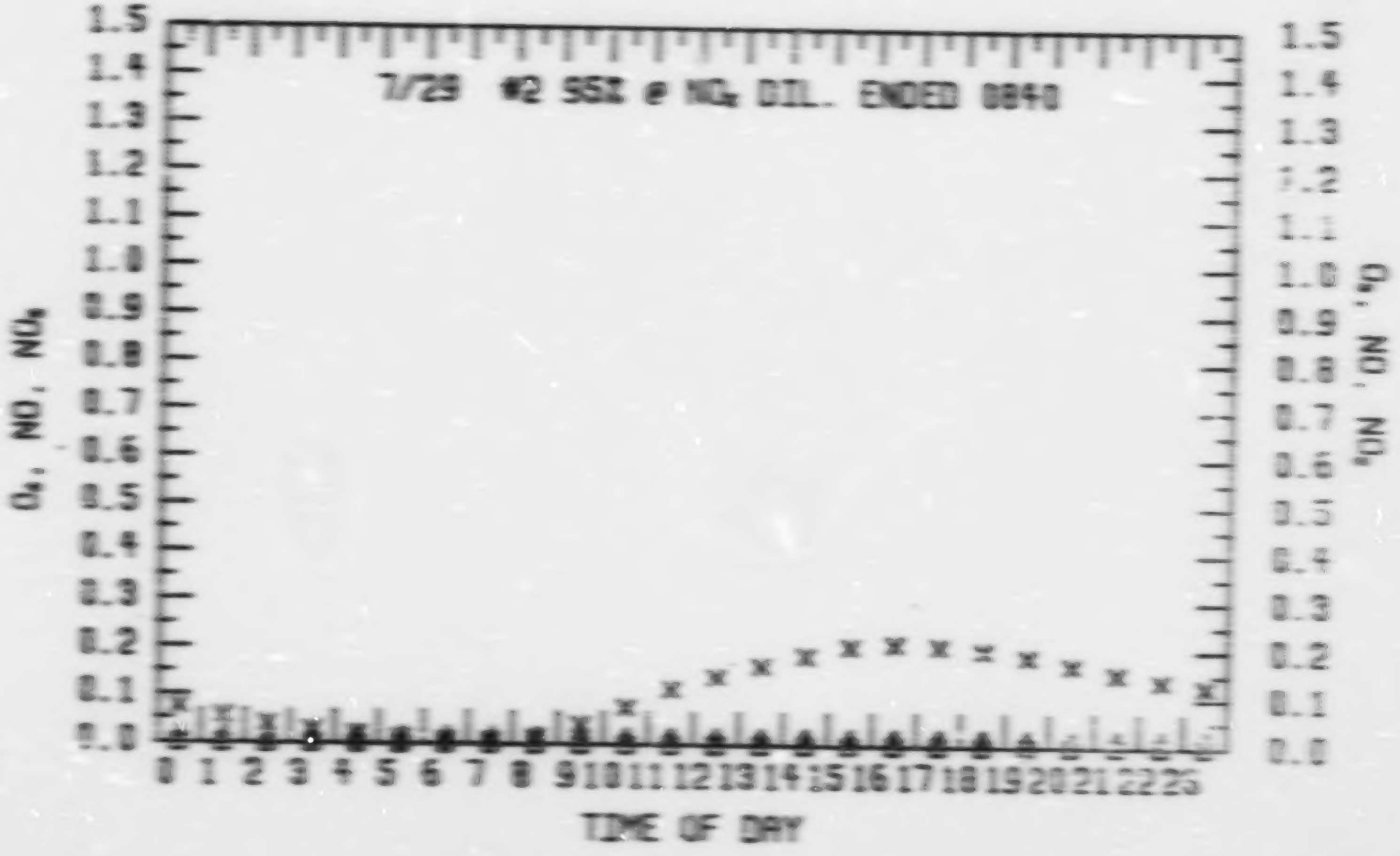


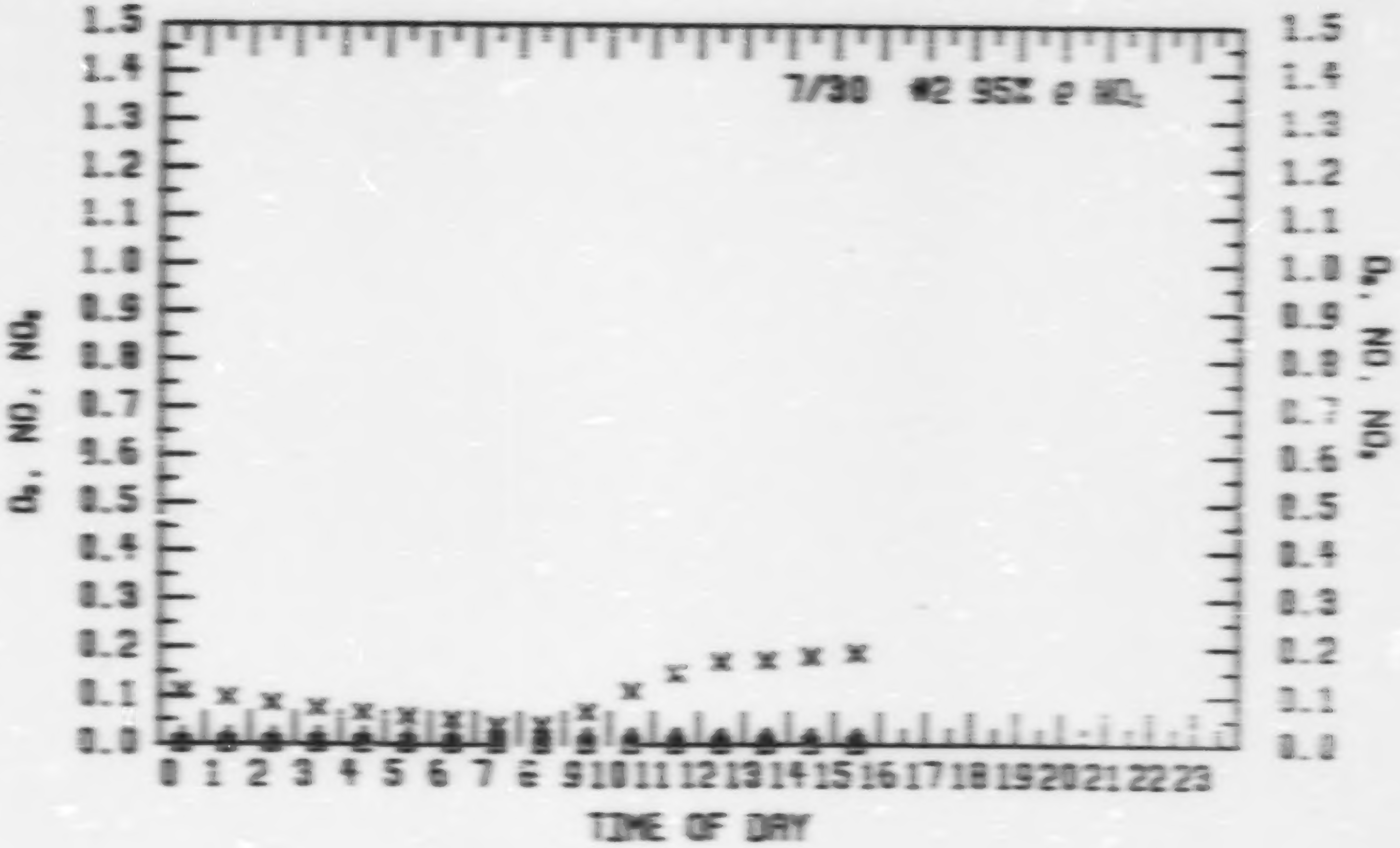
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#1 7/28
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

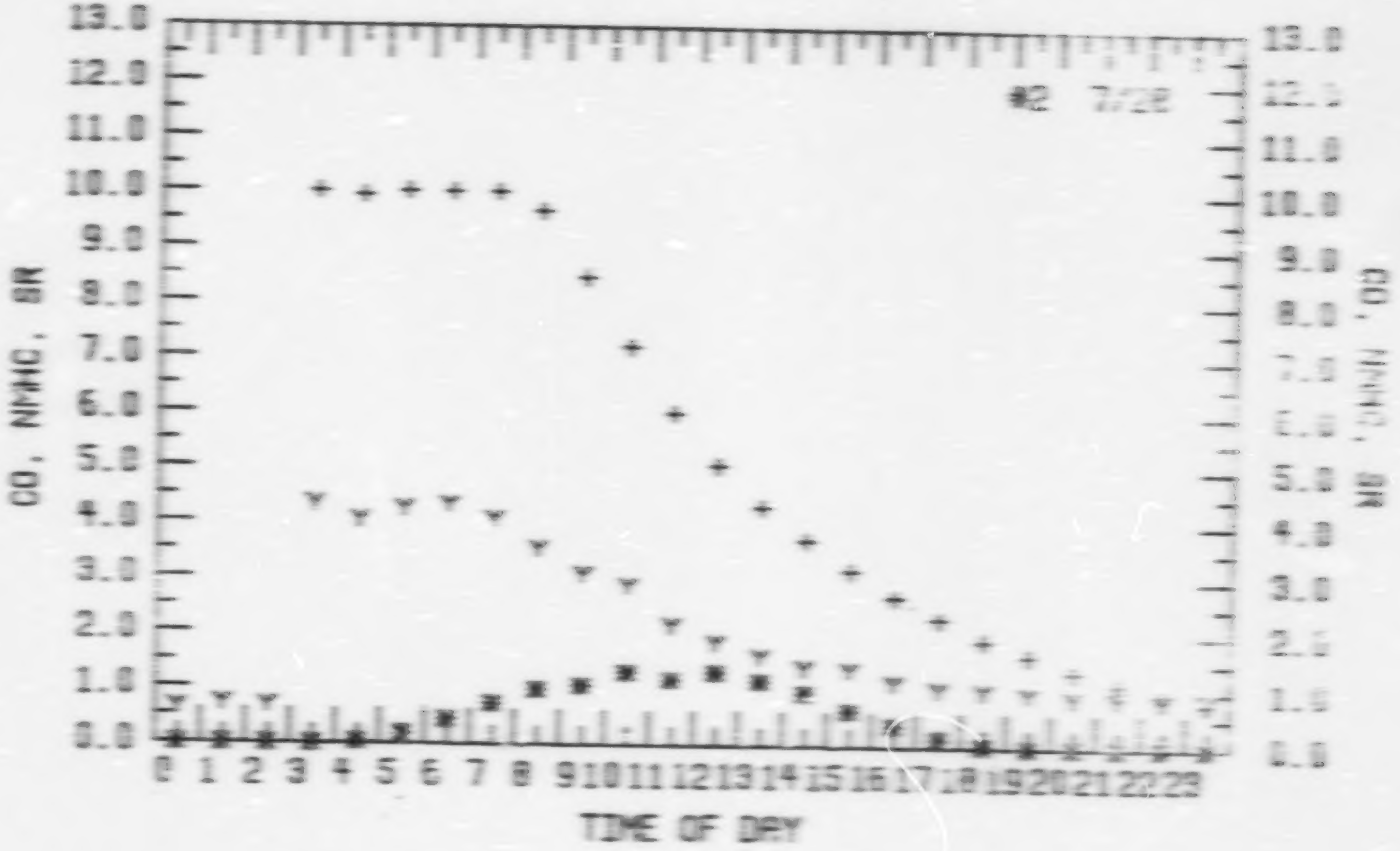

13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
#1 7/29
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

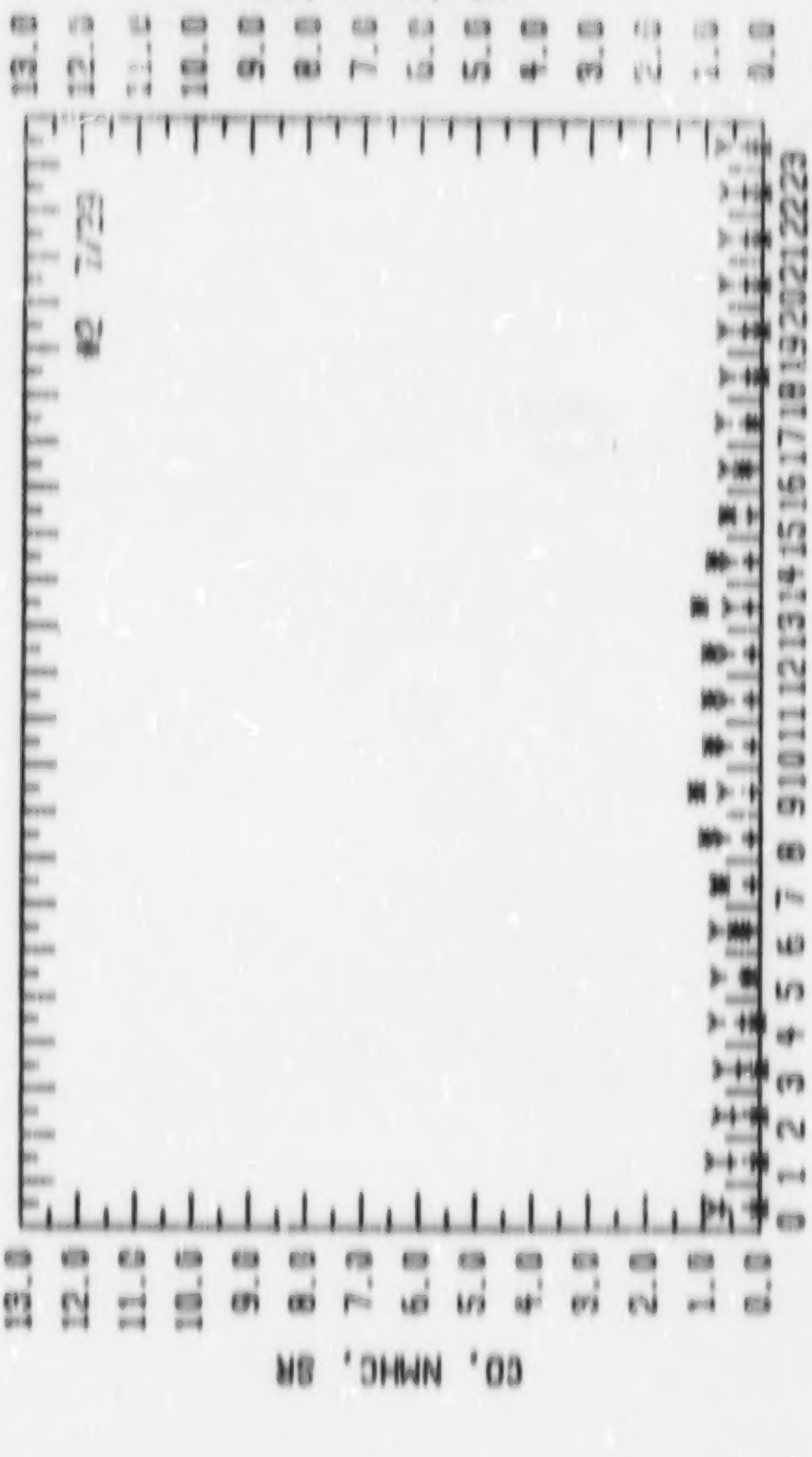

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.5
1.5
0.0
#1 7/25
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

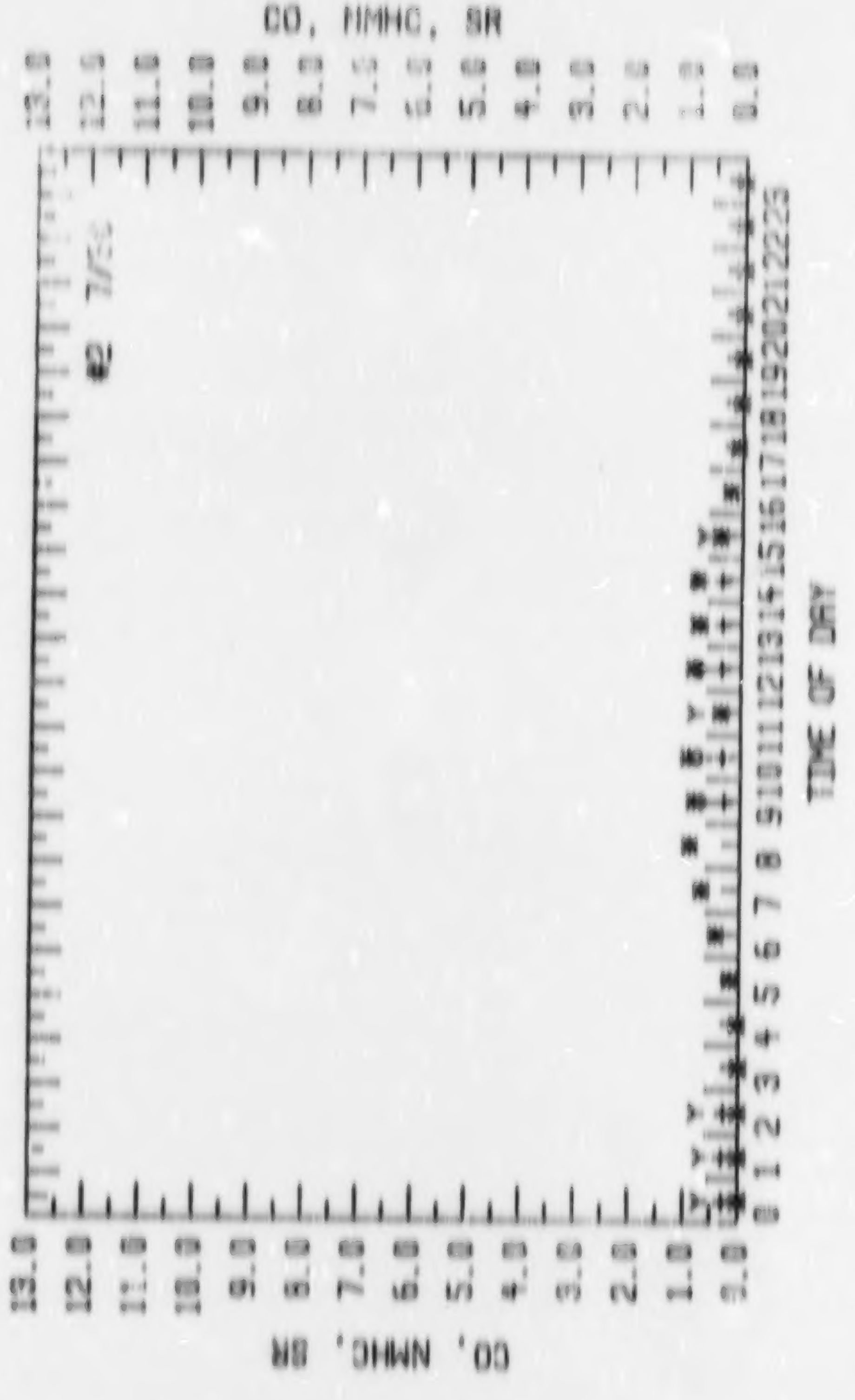

7/28 #2 95% @ NO$_x$ DIL. BEGAN 0840
O_3, NO, NO$_x$
O_3, NO, NO$_x$
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

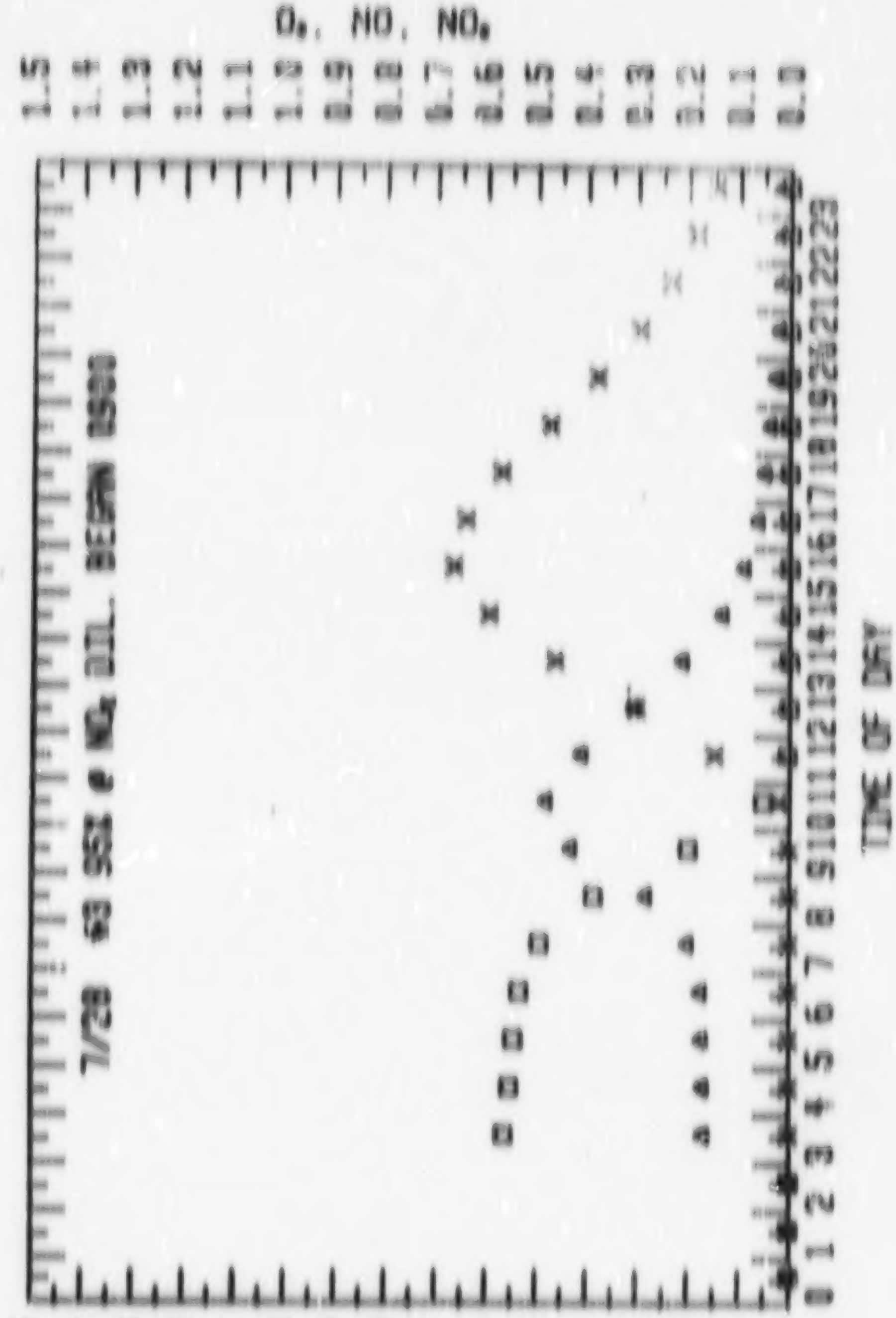

7/28 #2 55% @ NO$_x$ DIL. ENDED 0840
O$_3$, NO, NO$_2$
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
O$_3$, NO, NO$_2$

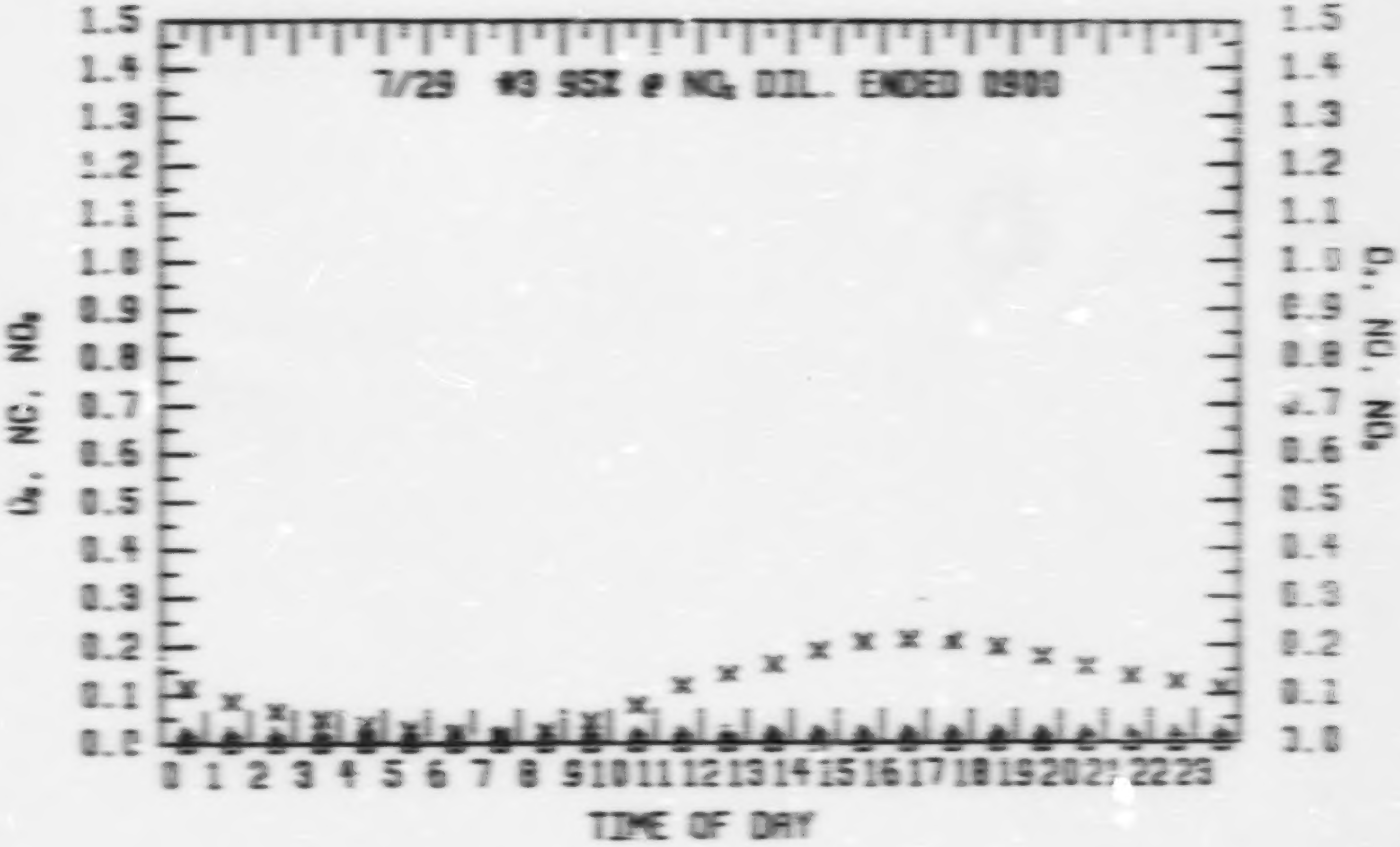

7/30 #2 95% @ NO₂
O₃, NO, NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

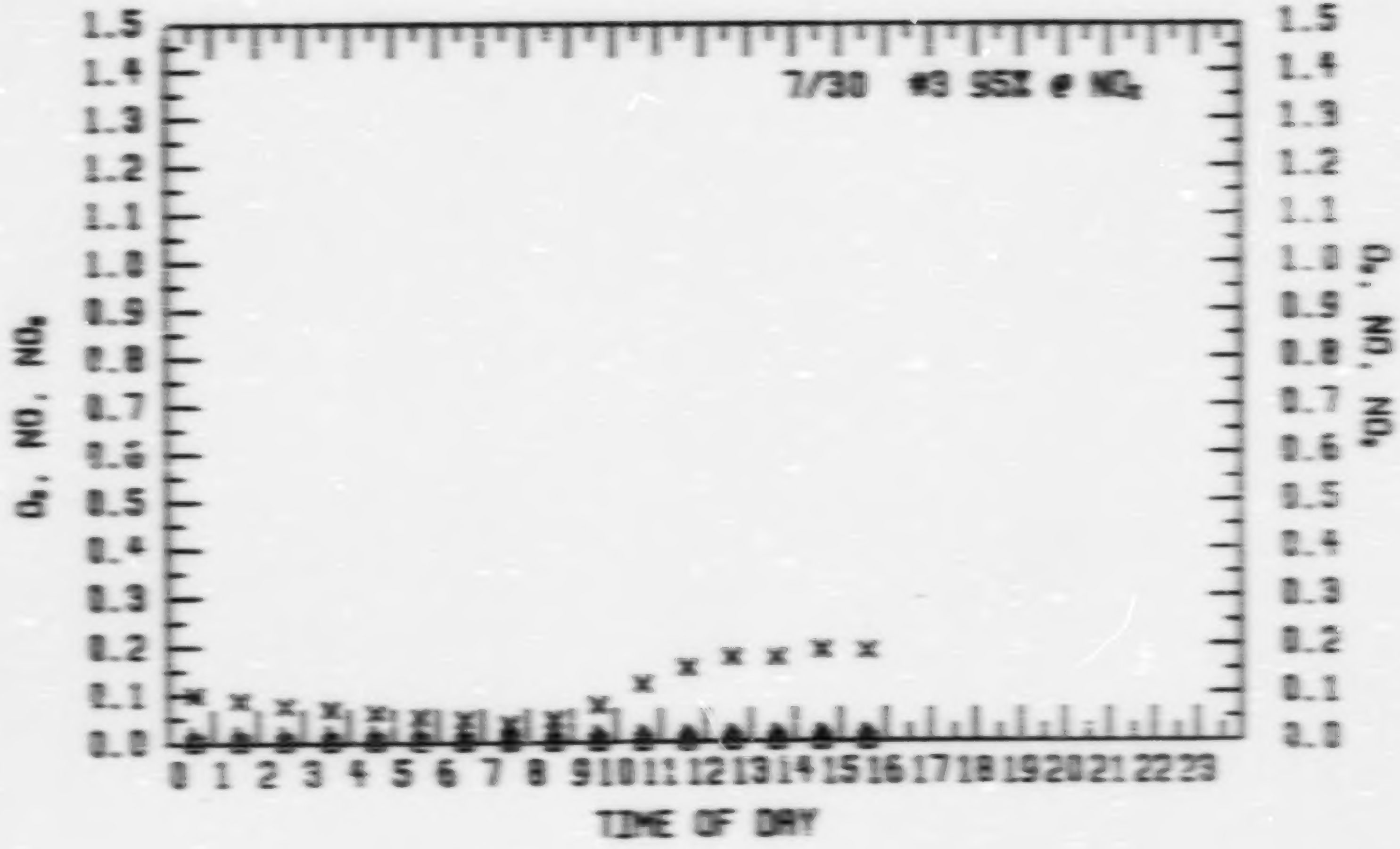

#2 7/28
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
13.0
12.5
11.0
10.0
9.0
8.0
7.5
6.0
5.0
4.0
3.0
2.5
1.5
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

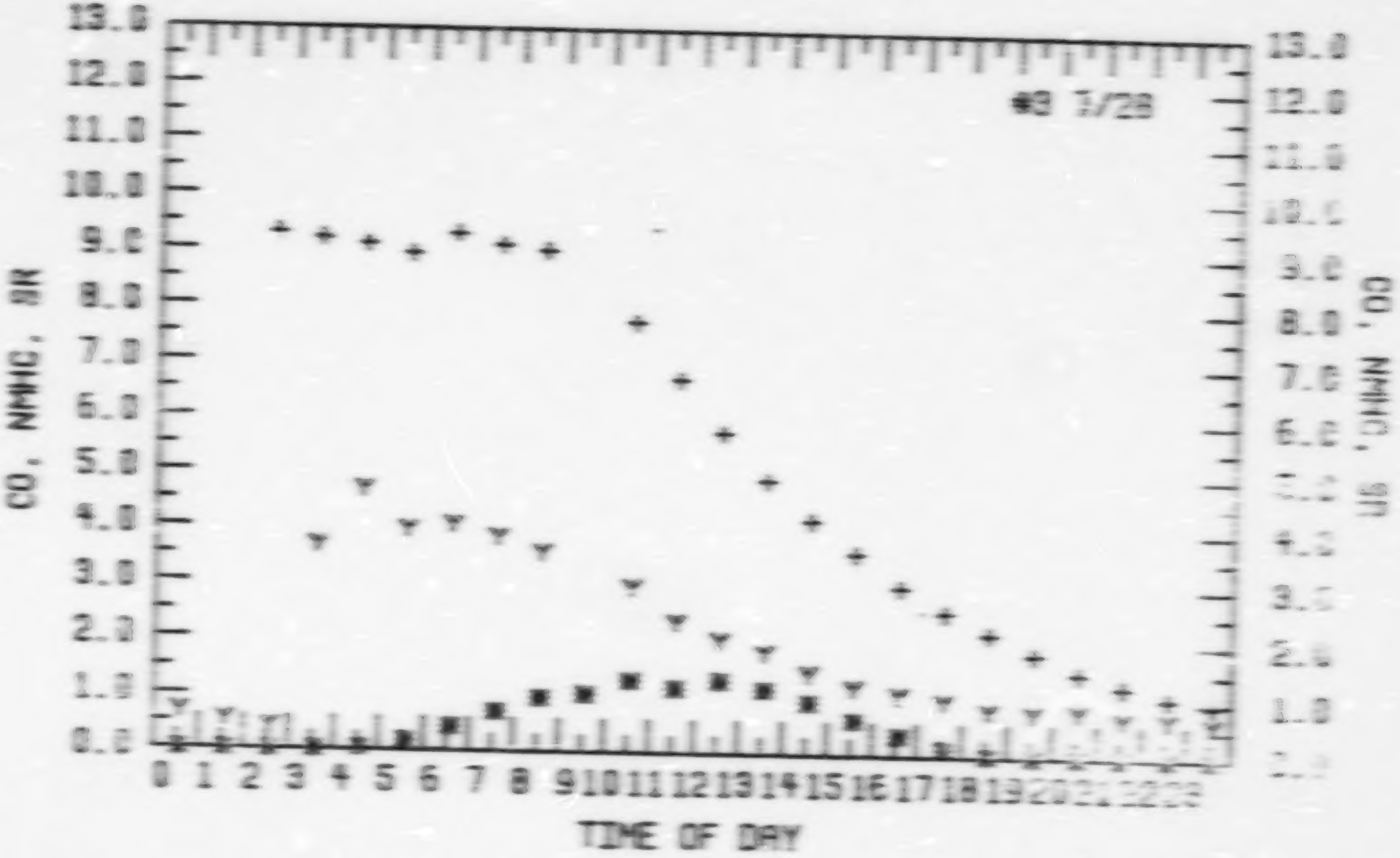

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#2 7/29
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

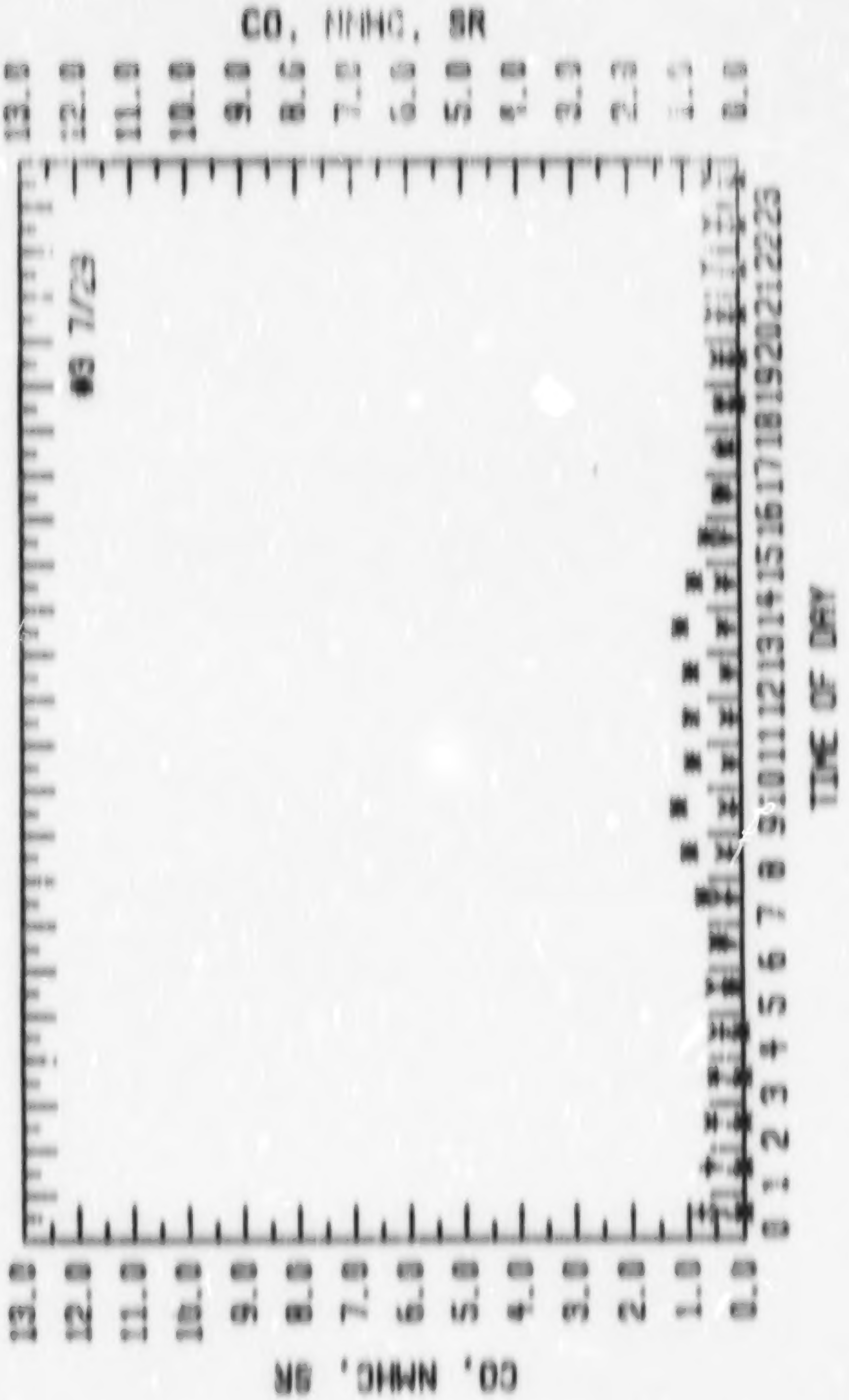

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#2 7/5
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR

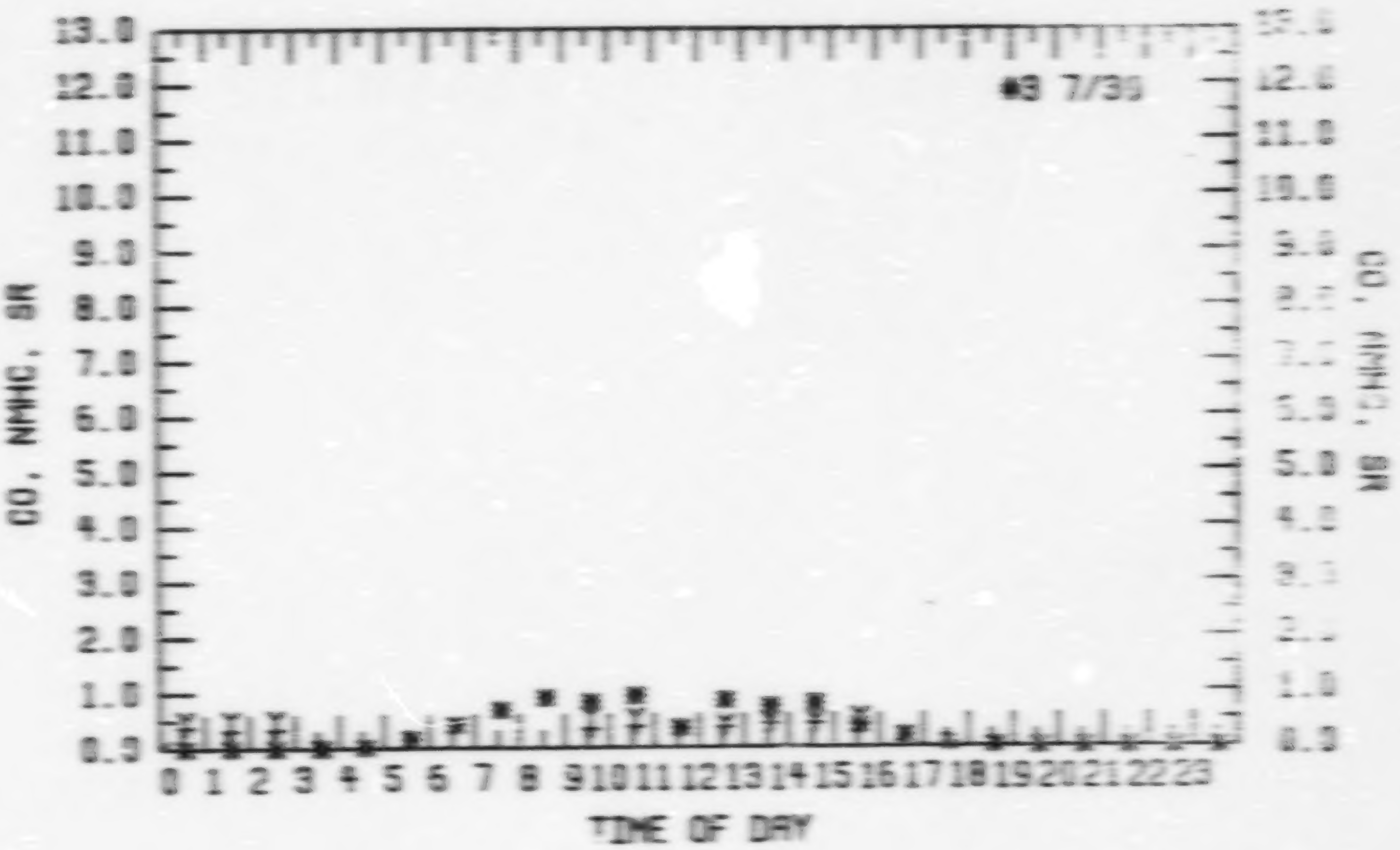

7/28 #3 SSE @ NO2 DIL. BEGAN 0500
O3, NO, NO2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

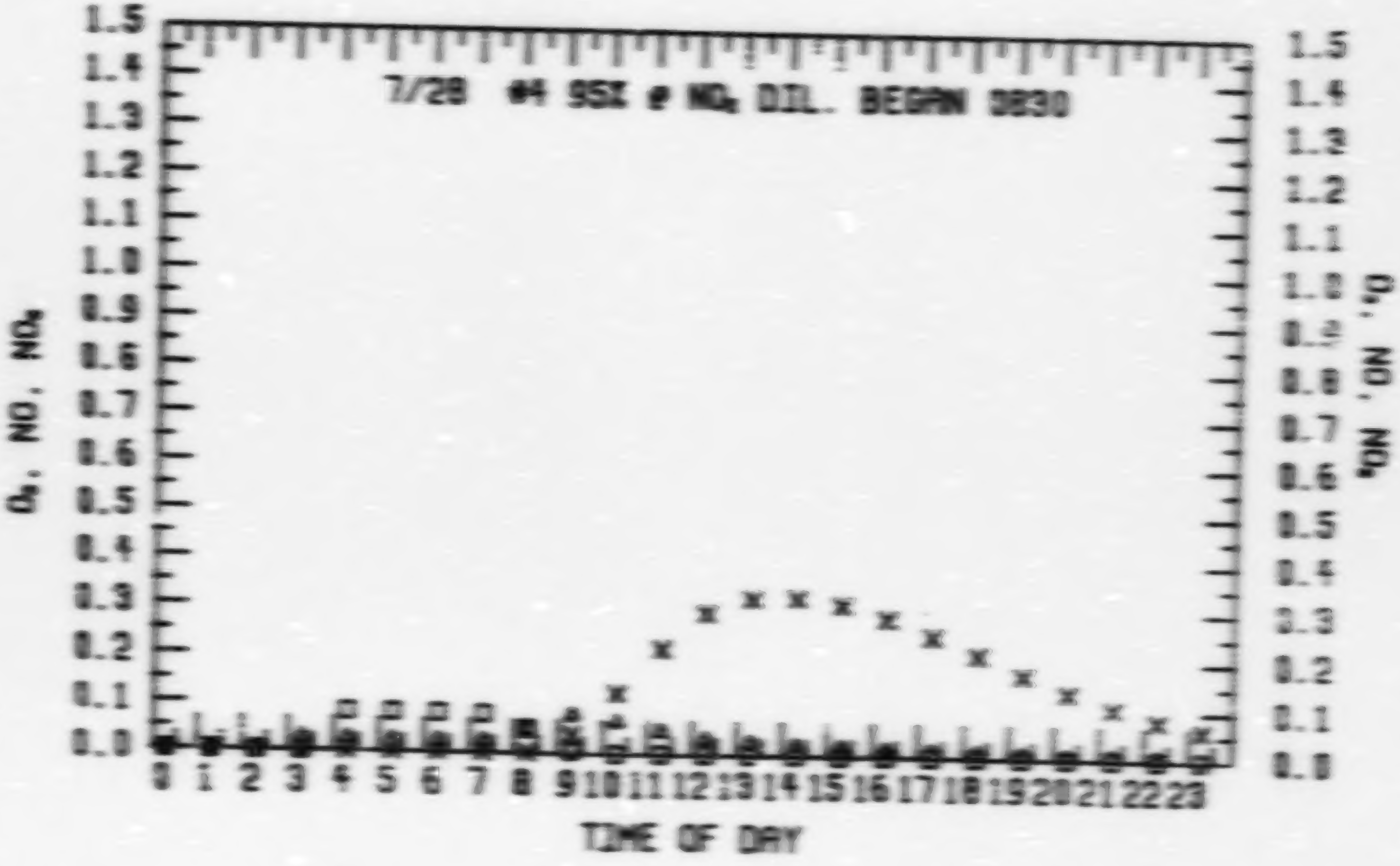

7/29 #3 95% @ NO_2 DIL. ENDED 0900
O_3, NO, NO_2
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

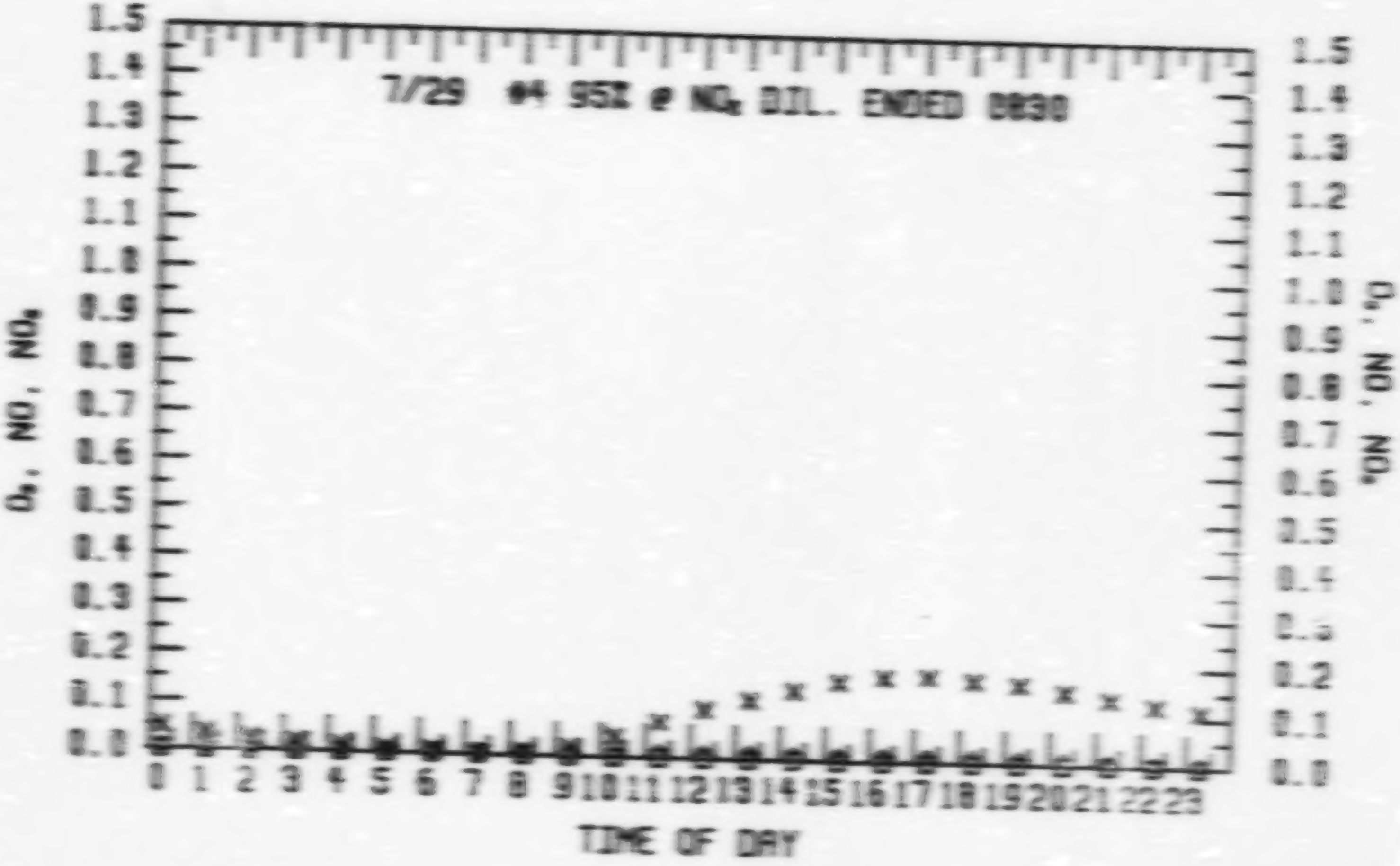
7/30 #3 SSE @ NO_2
O_3, NO, NO_2
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5

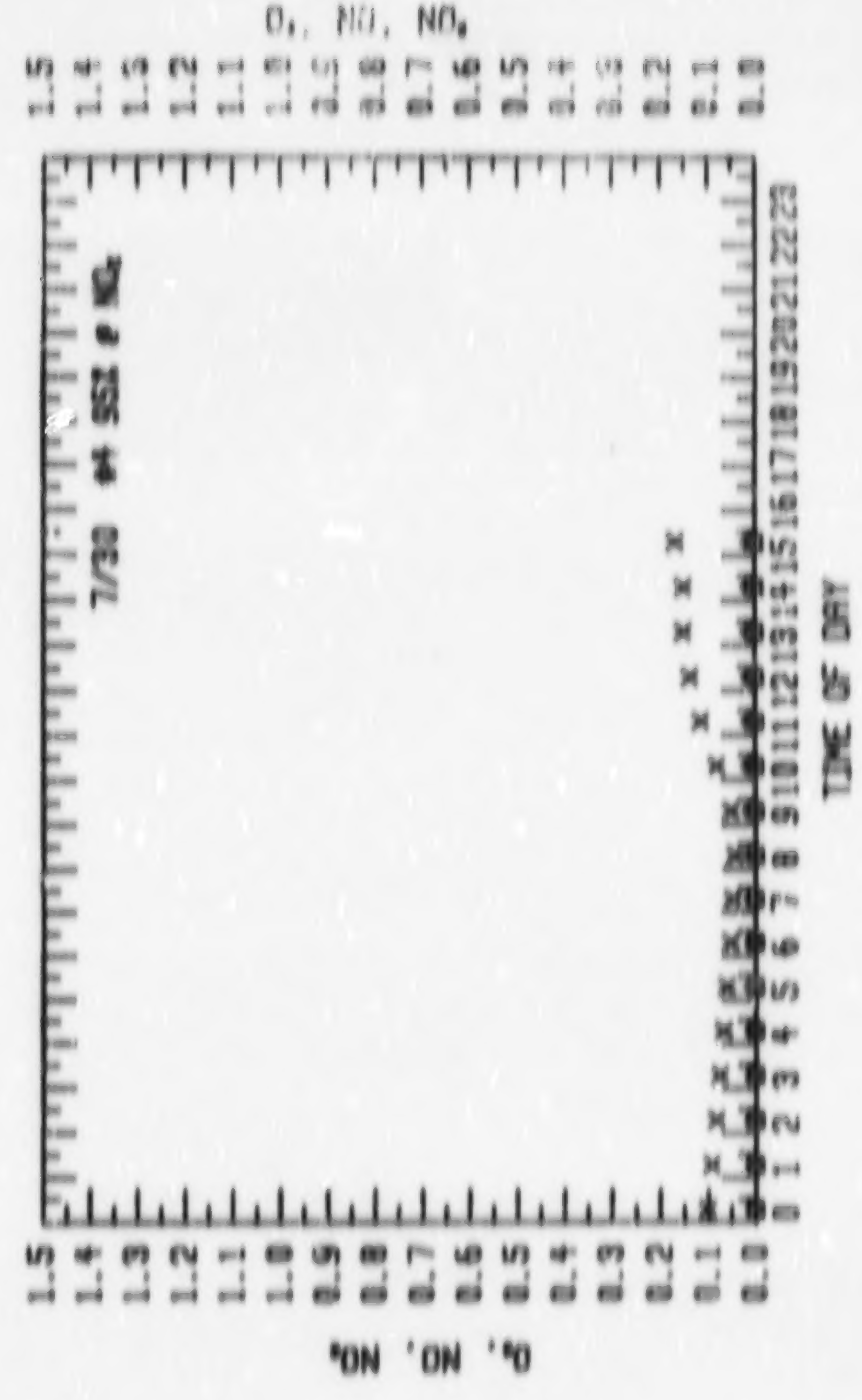

#3 1/28
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

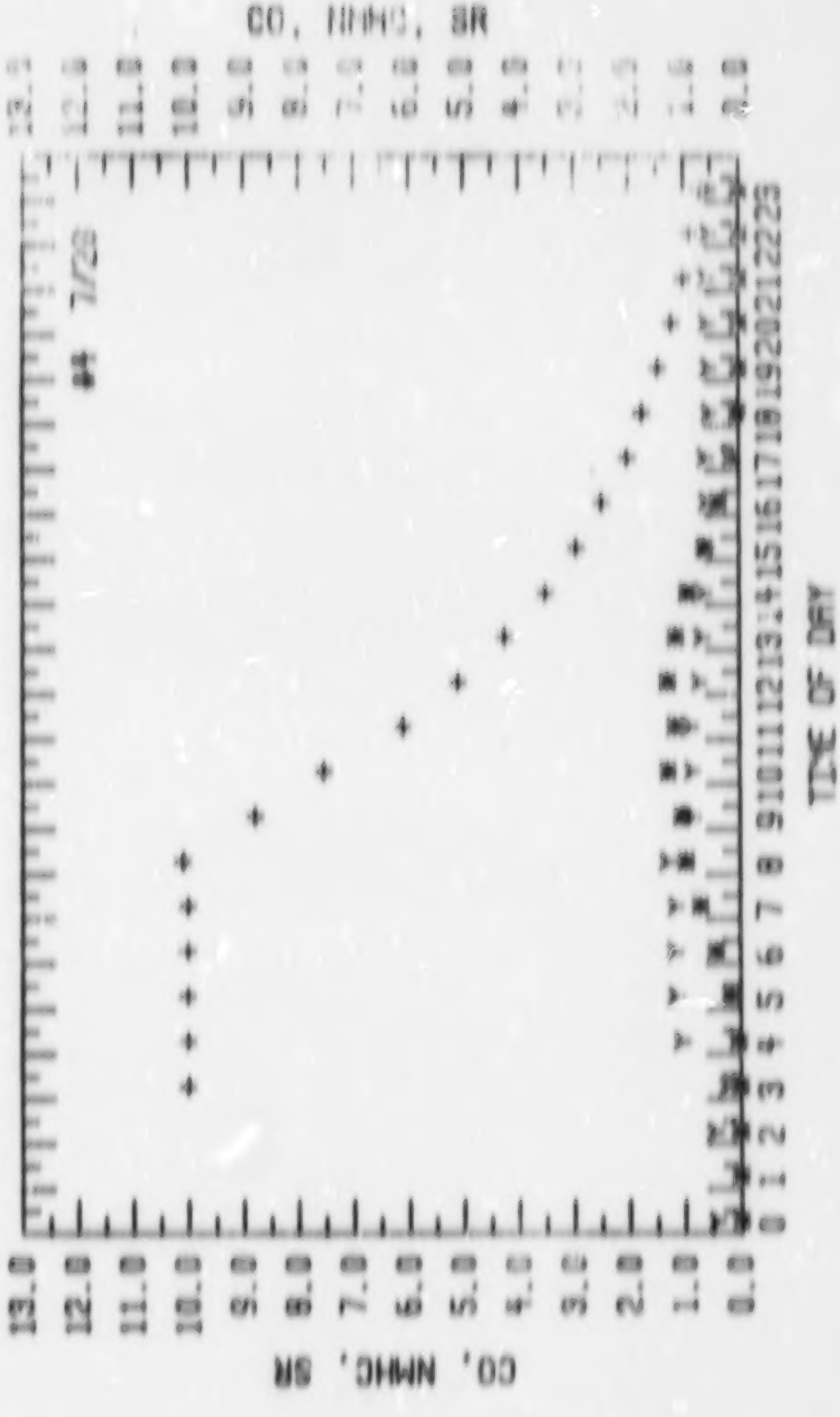

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#3 7/23
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

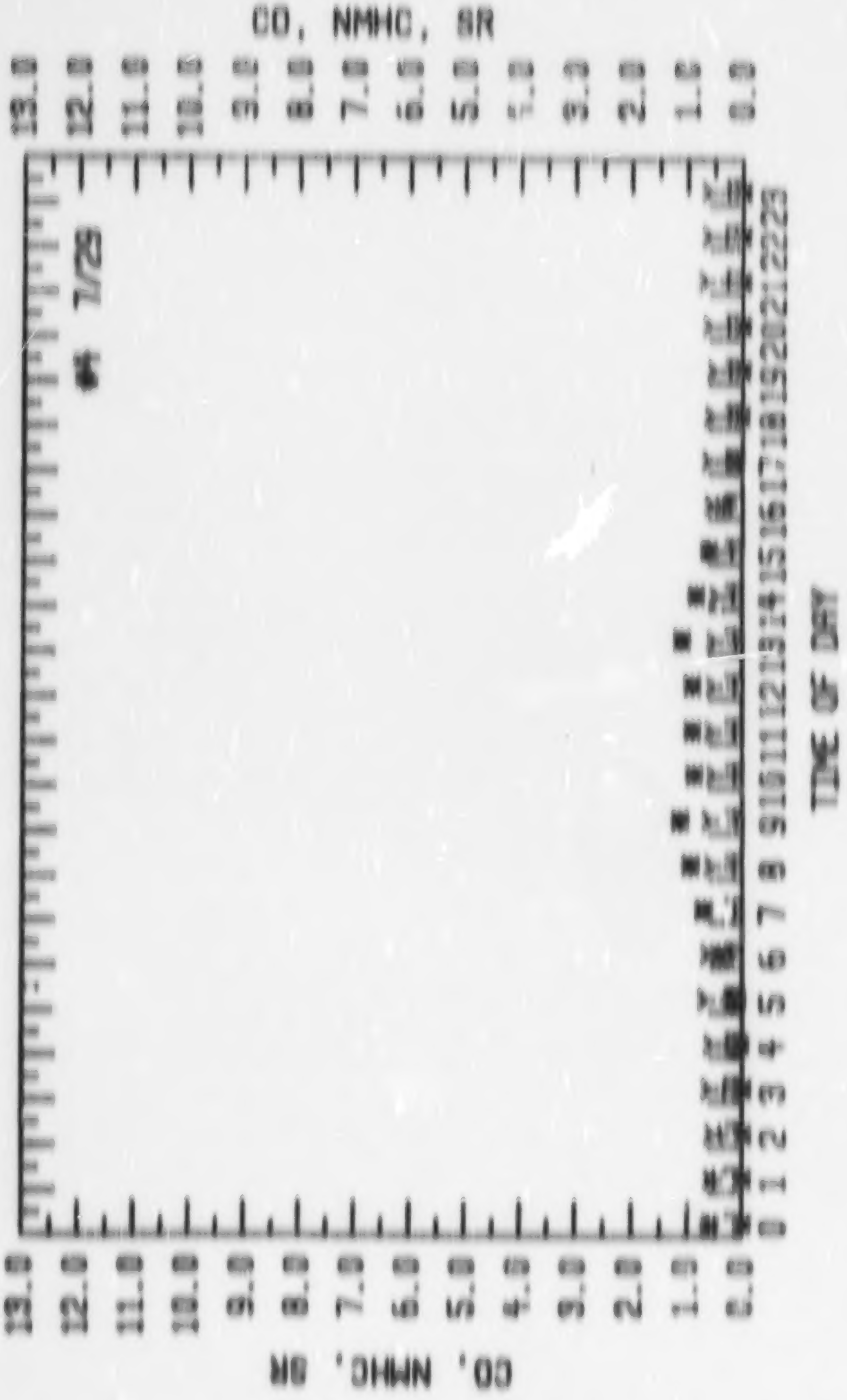

#3 7/30
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

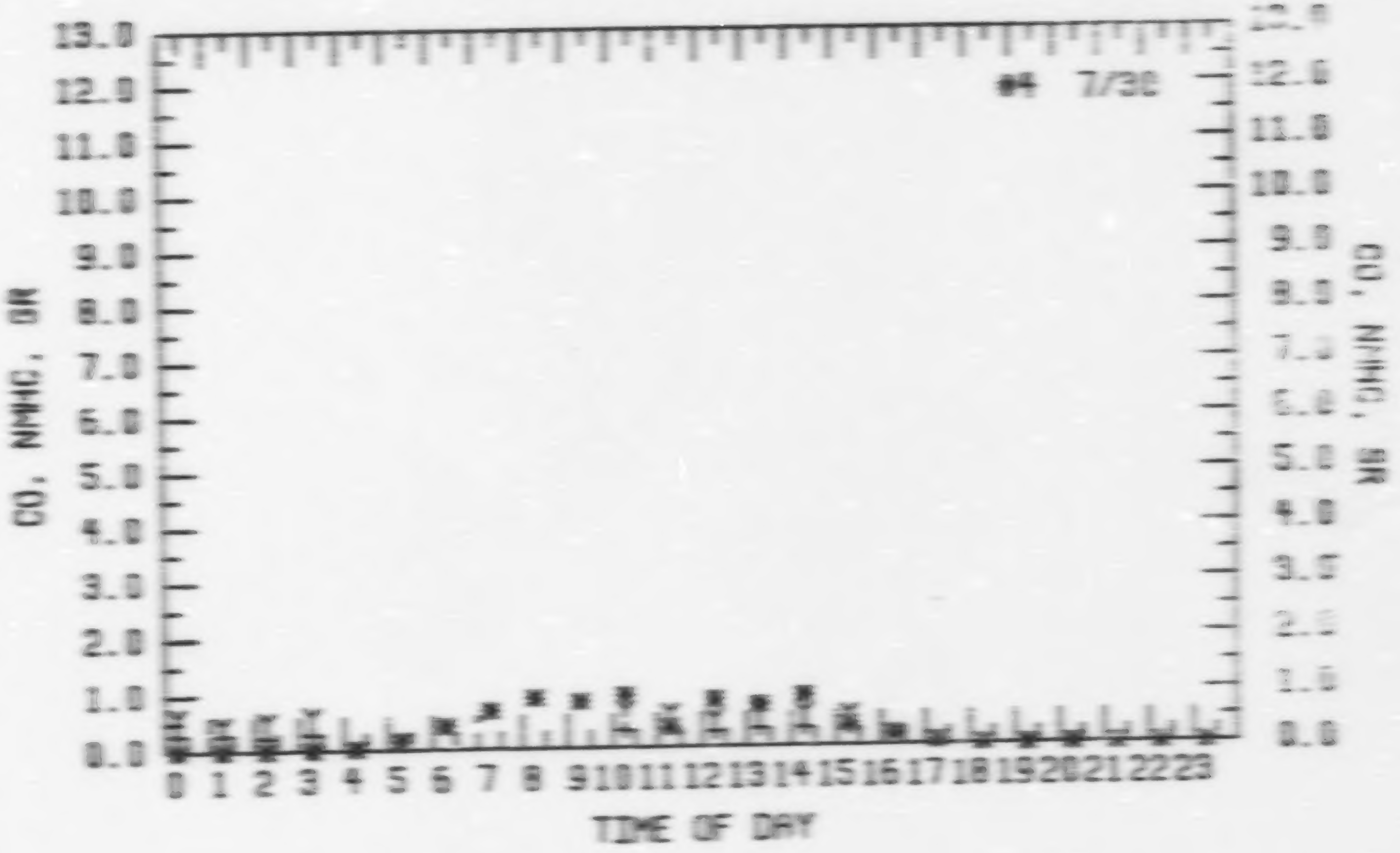

7/28 #4 95% @ NO₂ DIL. BEGAN 0830
O₃, NO, NO₂
O₃, NO, NO₂
TIME OF DAY
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

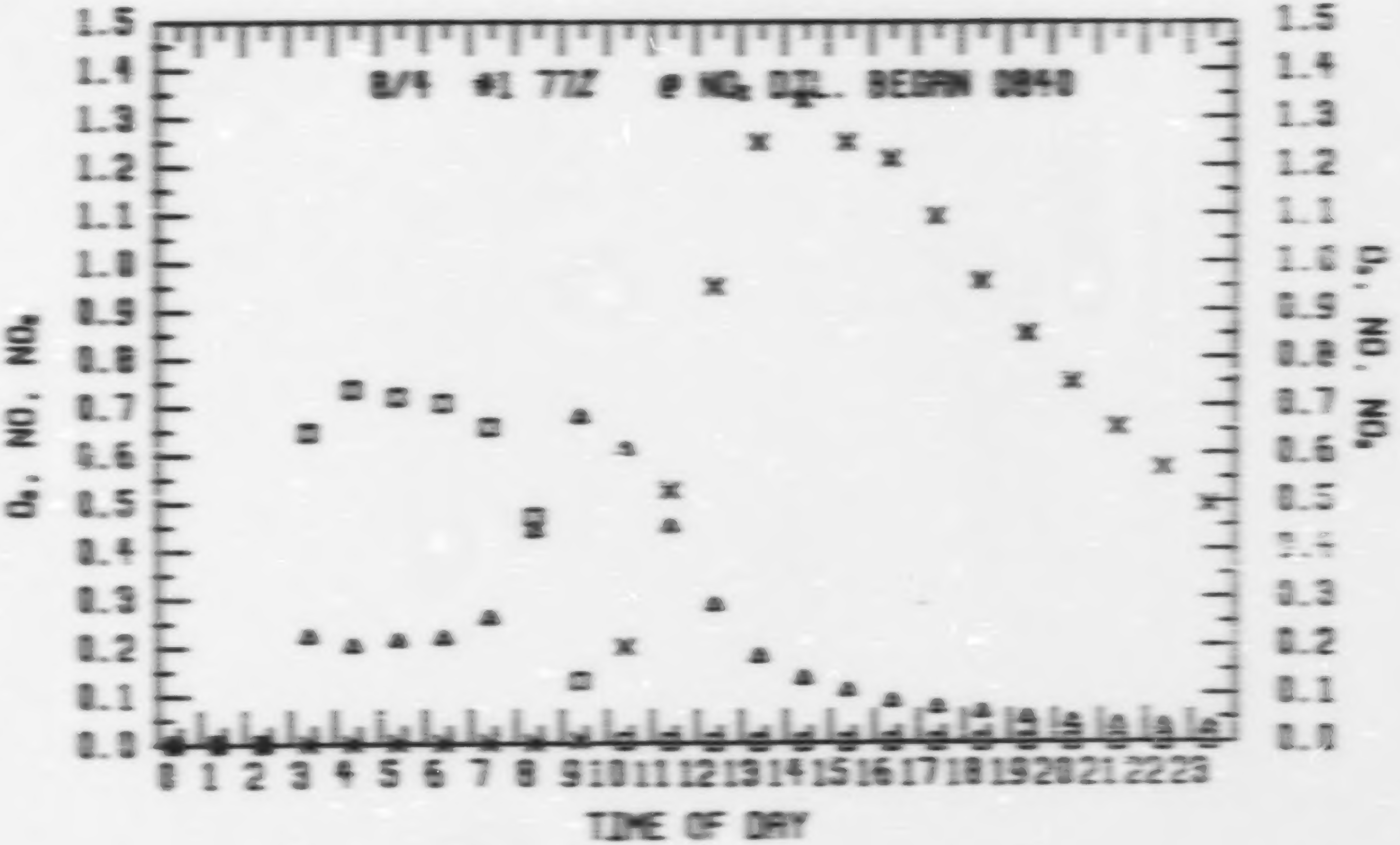

7/29 #4 95% @ NO₂ DIL. ENDED 0830
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

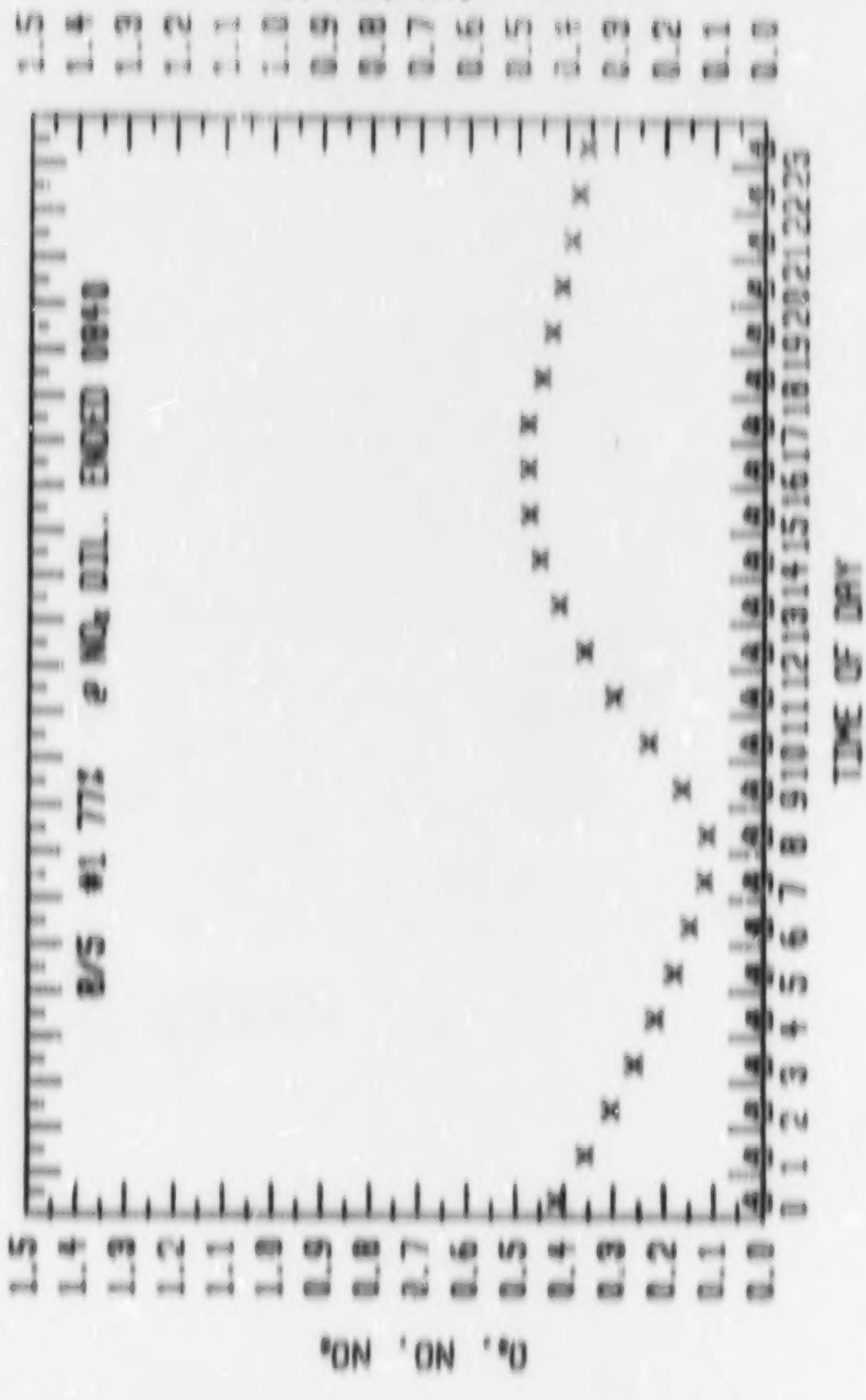

7/30 #4 SSI # NO2
O3, NO, NO2
TIME OF DAY
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
x

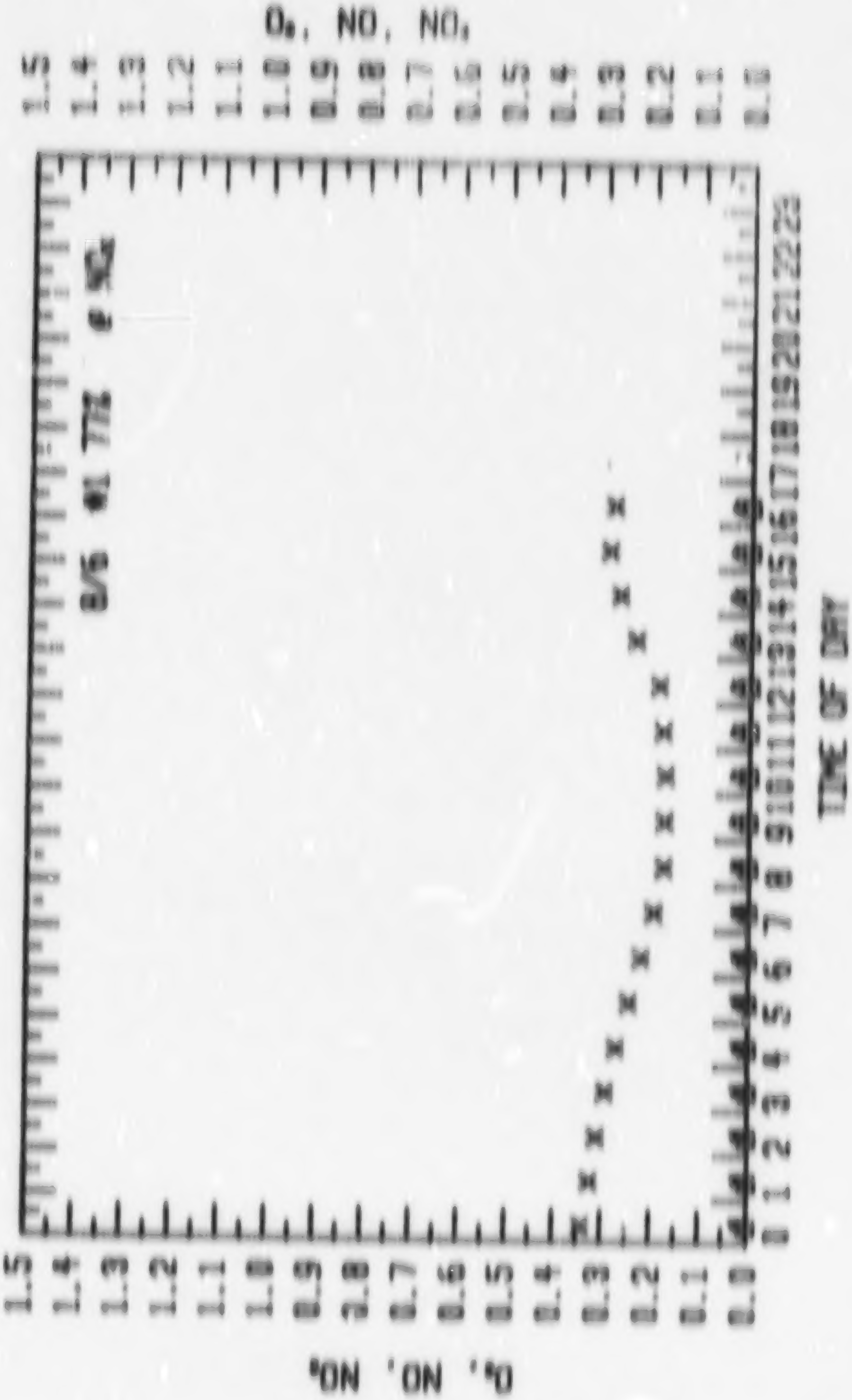

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#4 7/28
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR

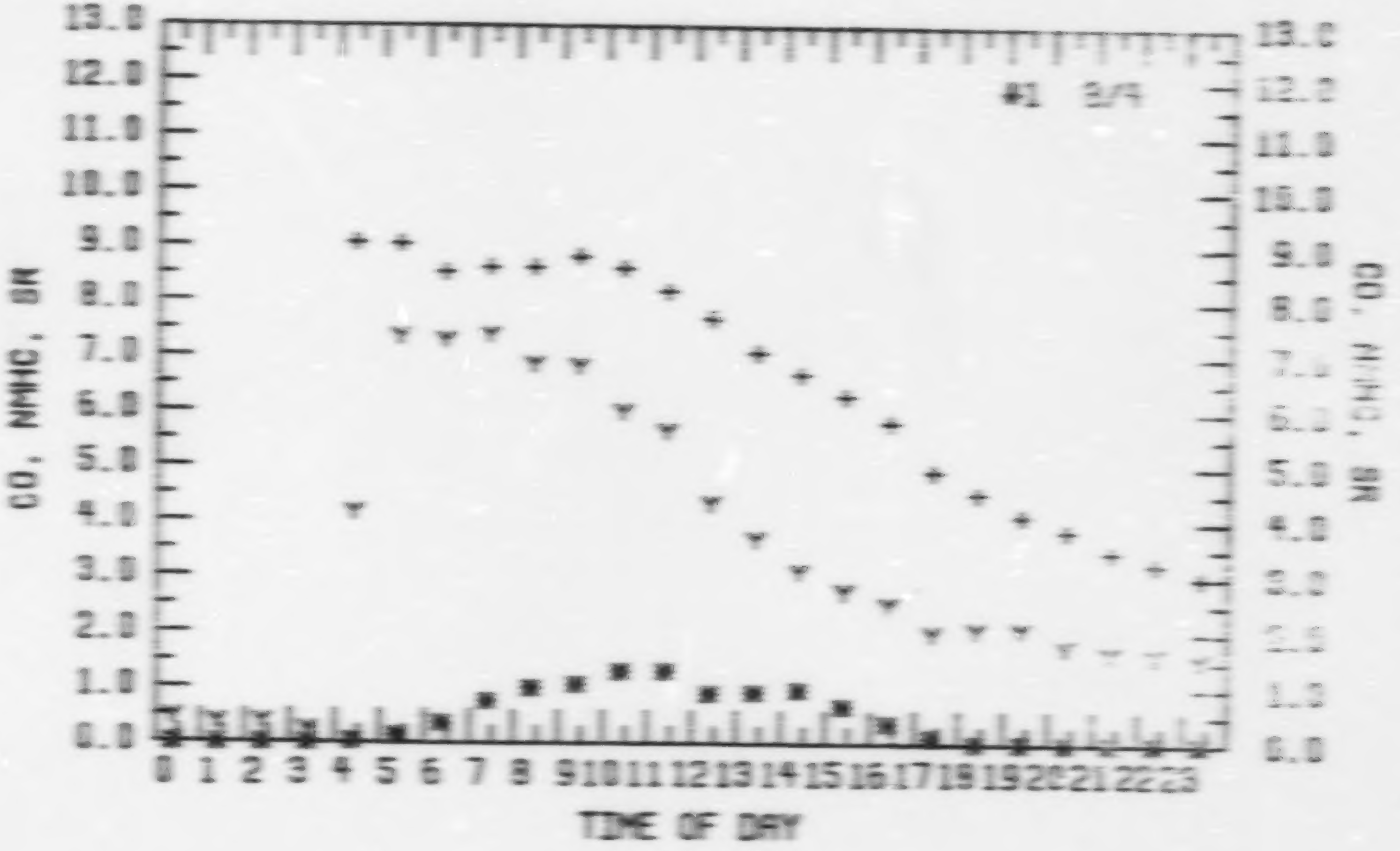

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#4 7/28
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

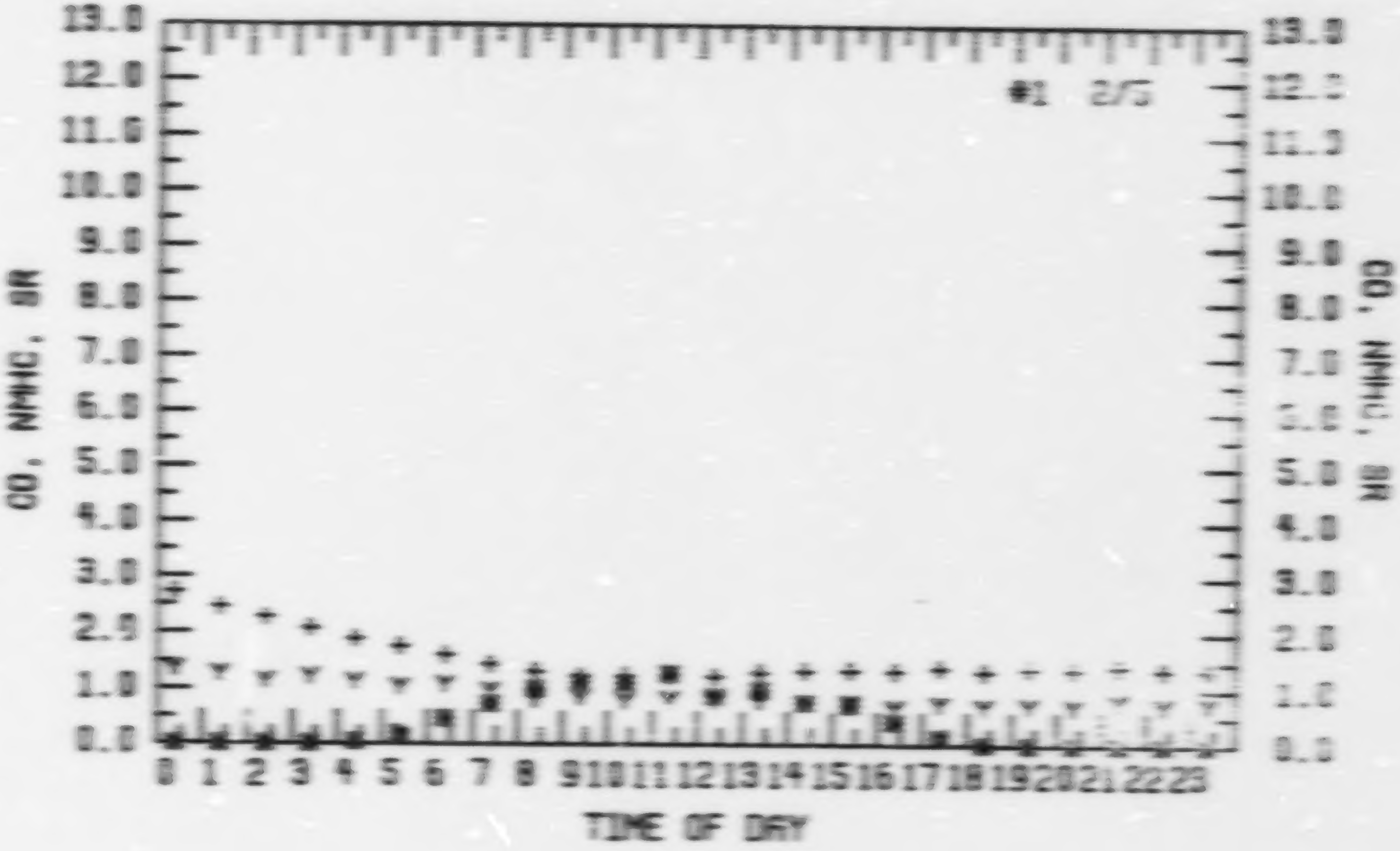

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#4 7/30
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

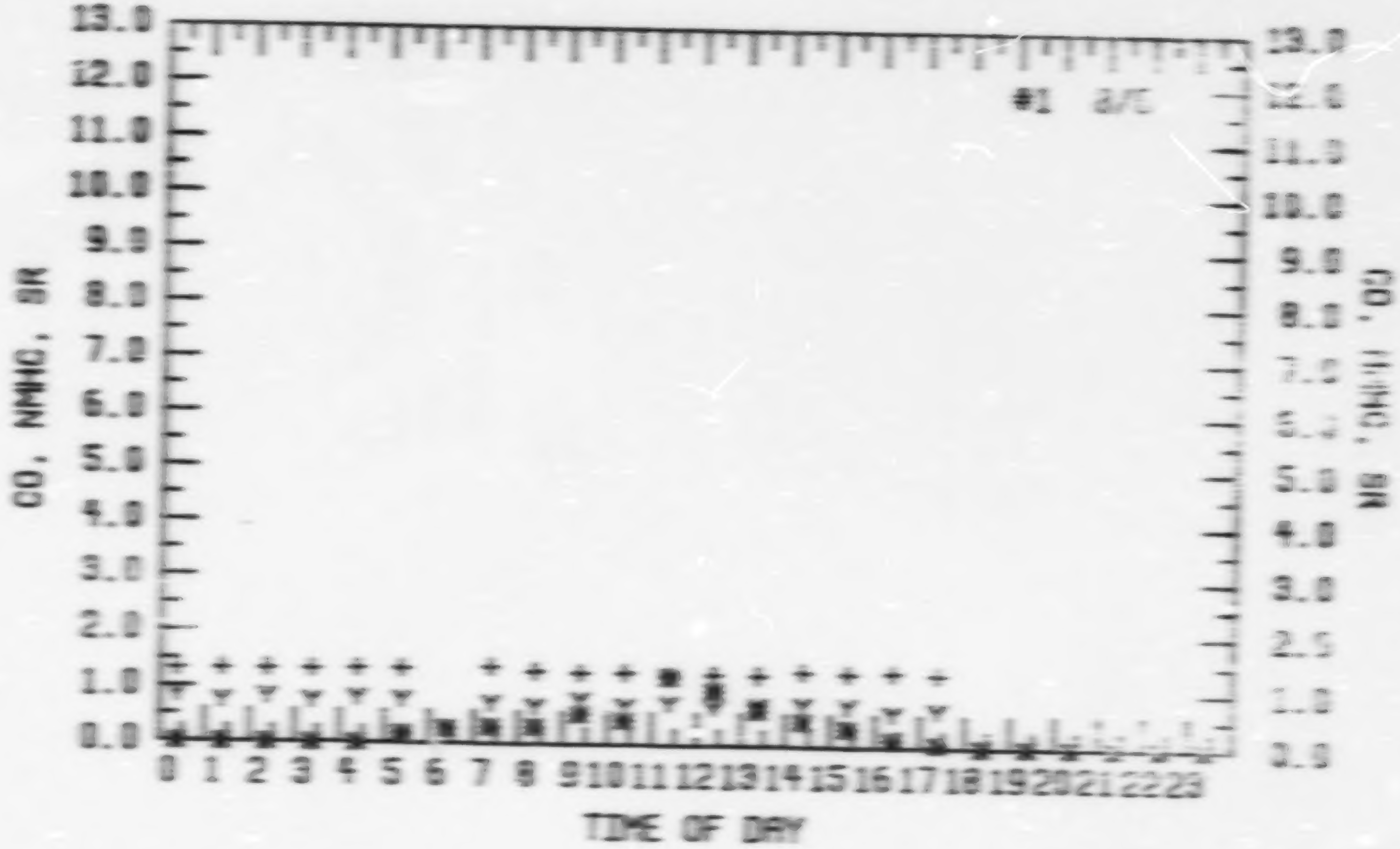

8/4 #1 77Z @ NO2 DIL. BEGAN 0840
O3, NO, NO2
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5

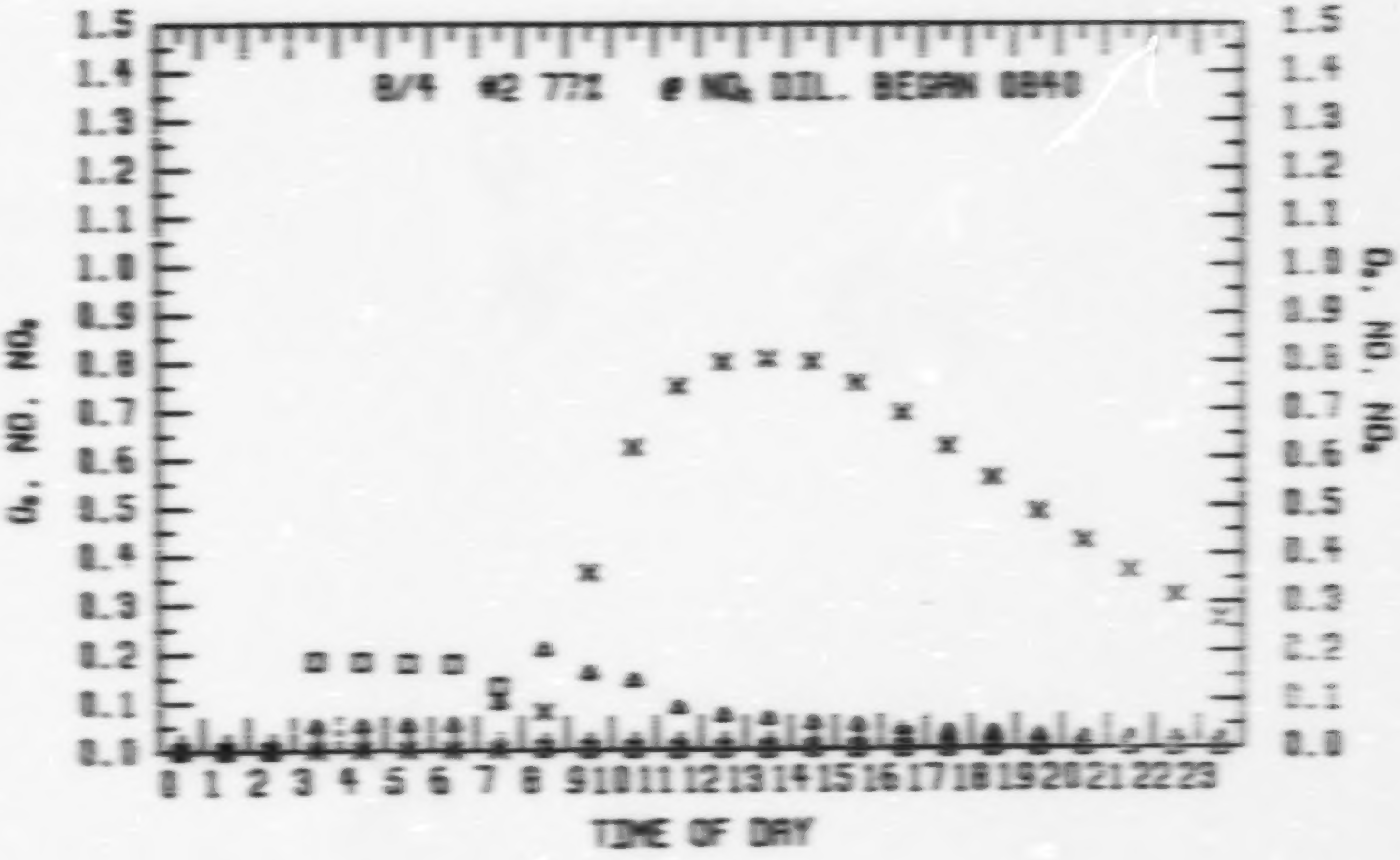

B/S #1 77% @ NO2 DIL. EXCEED 0840
O3, NO, NO2
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

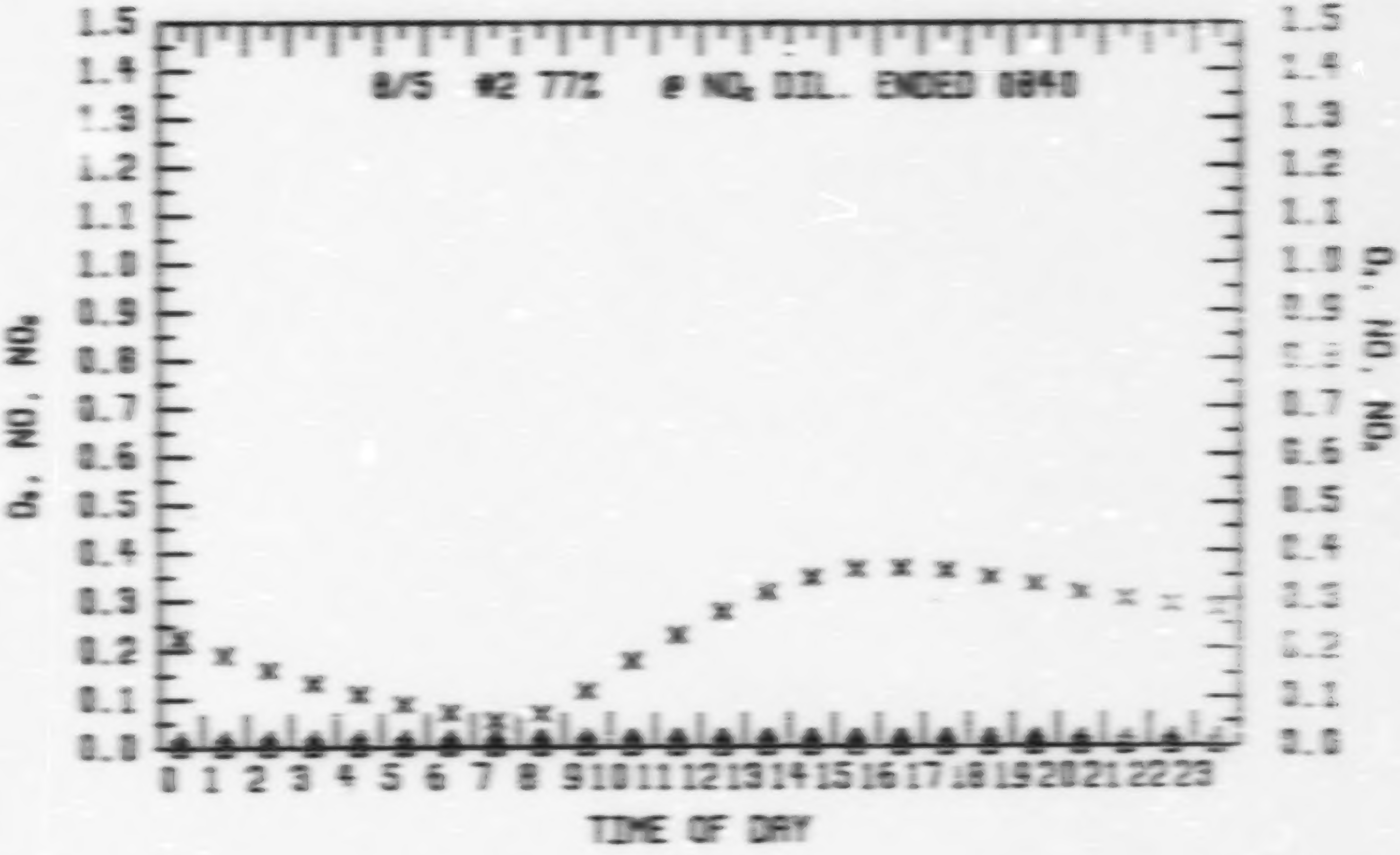

8/6 #1 TR2 # NO2
O3, NO, NO2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
O3, NO, NO2

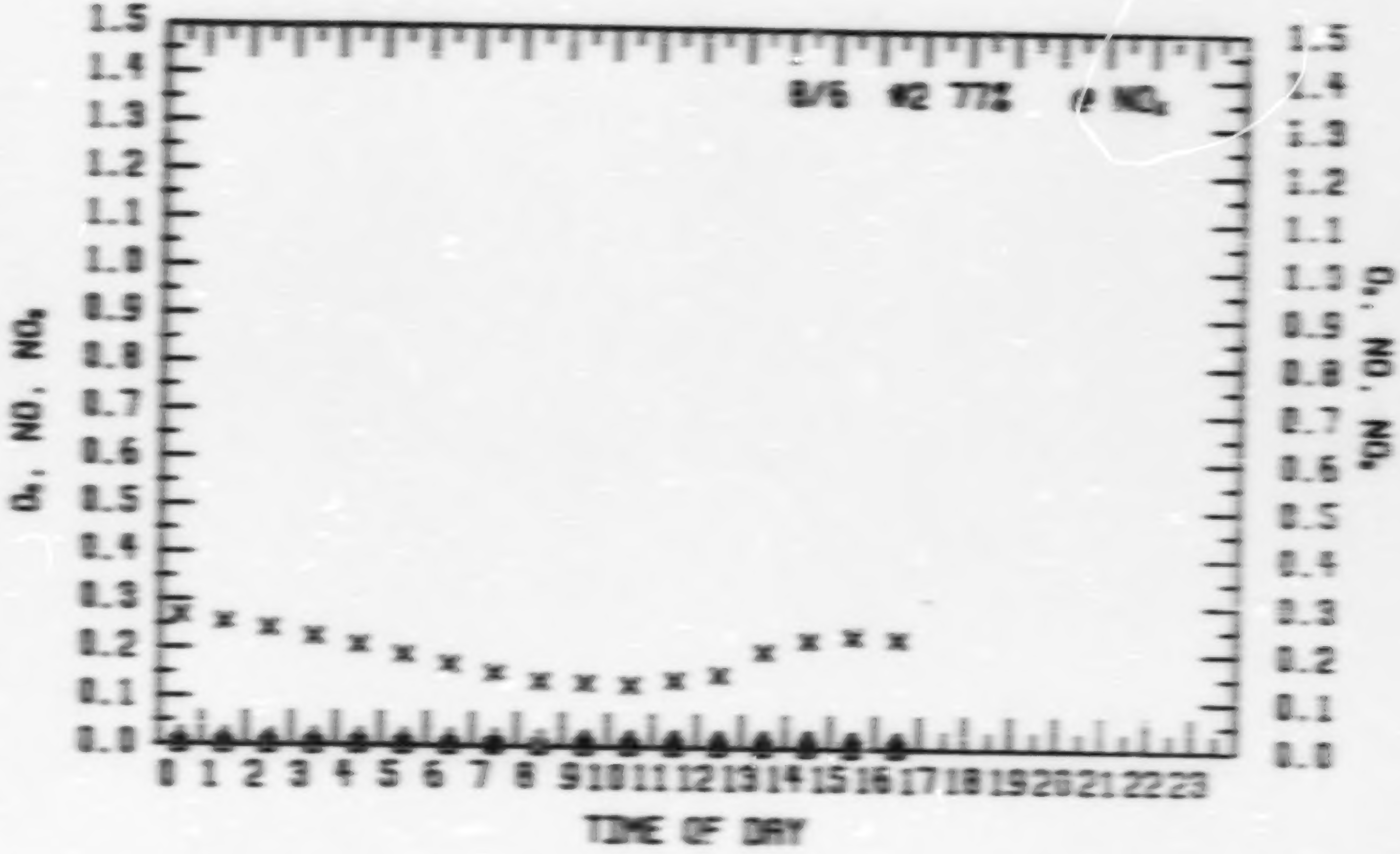

#1 3/4
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

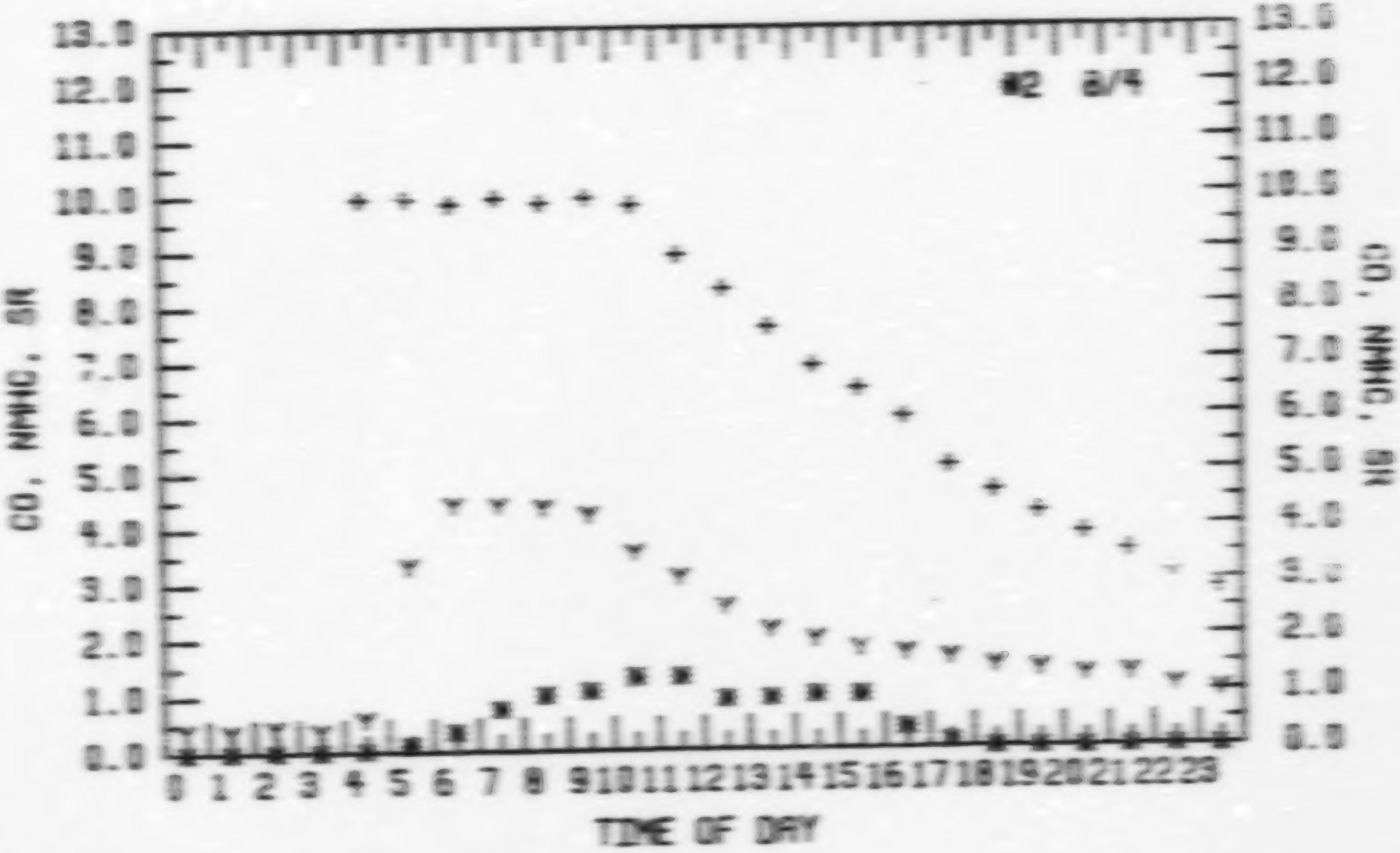

#1 2/5
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

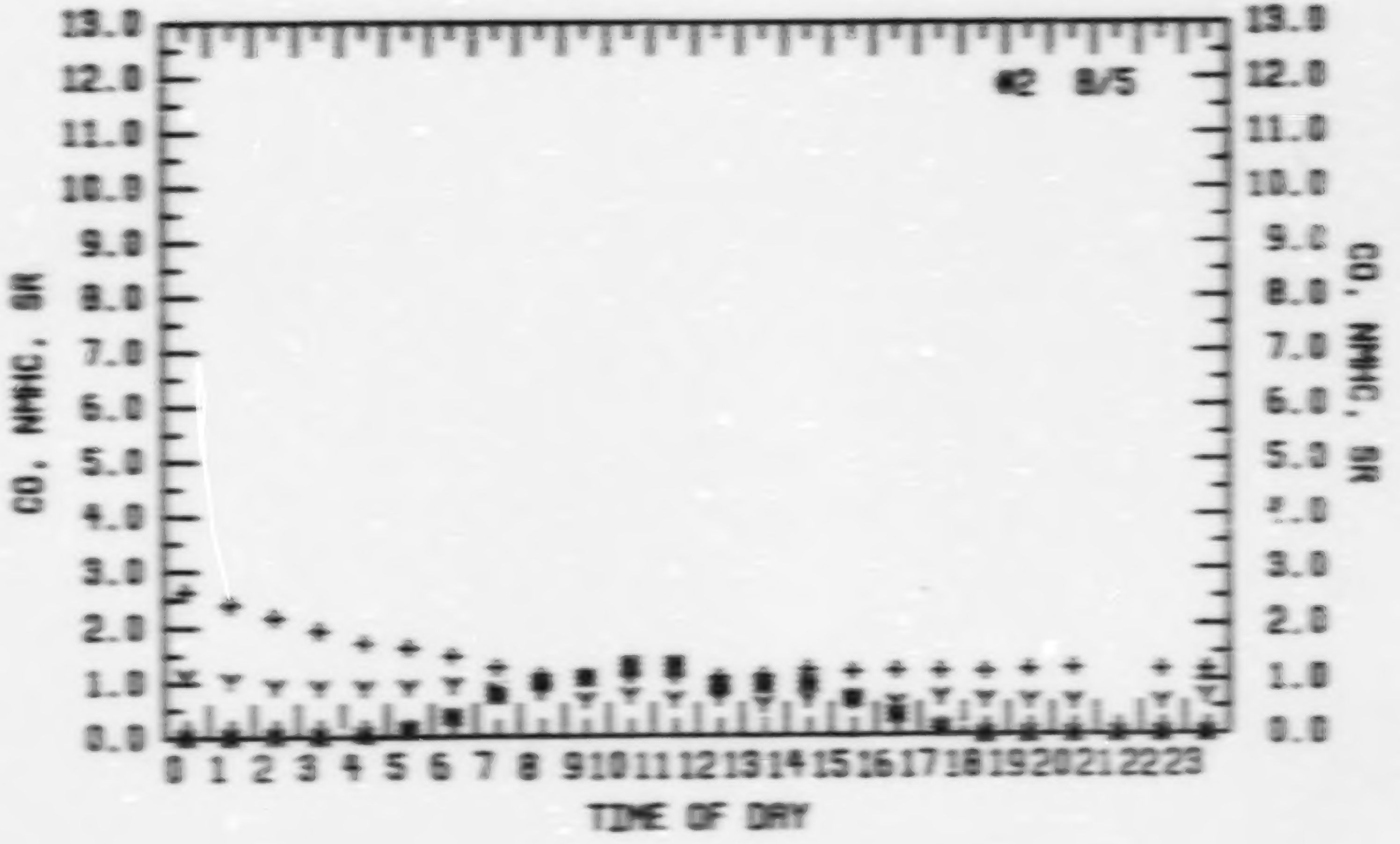

#1 2/C
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.5
1.0
0.0

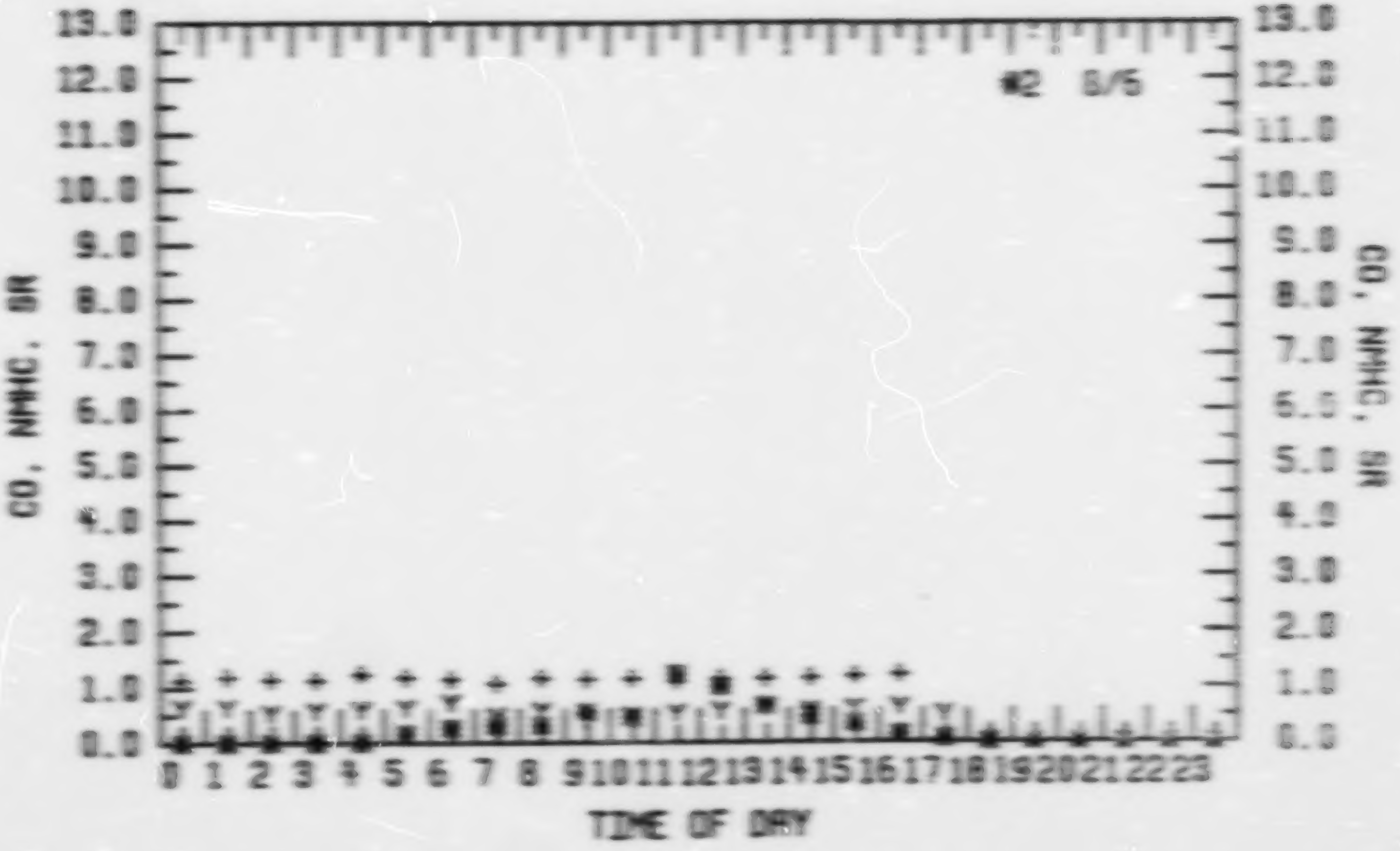

8/4 #2 77% @ NO₂ DIL. BEGAN 0840
O₃, NO, NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

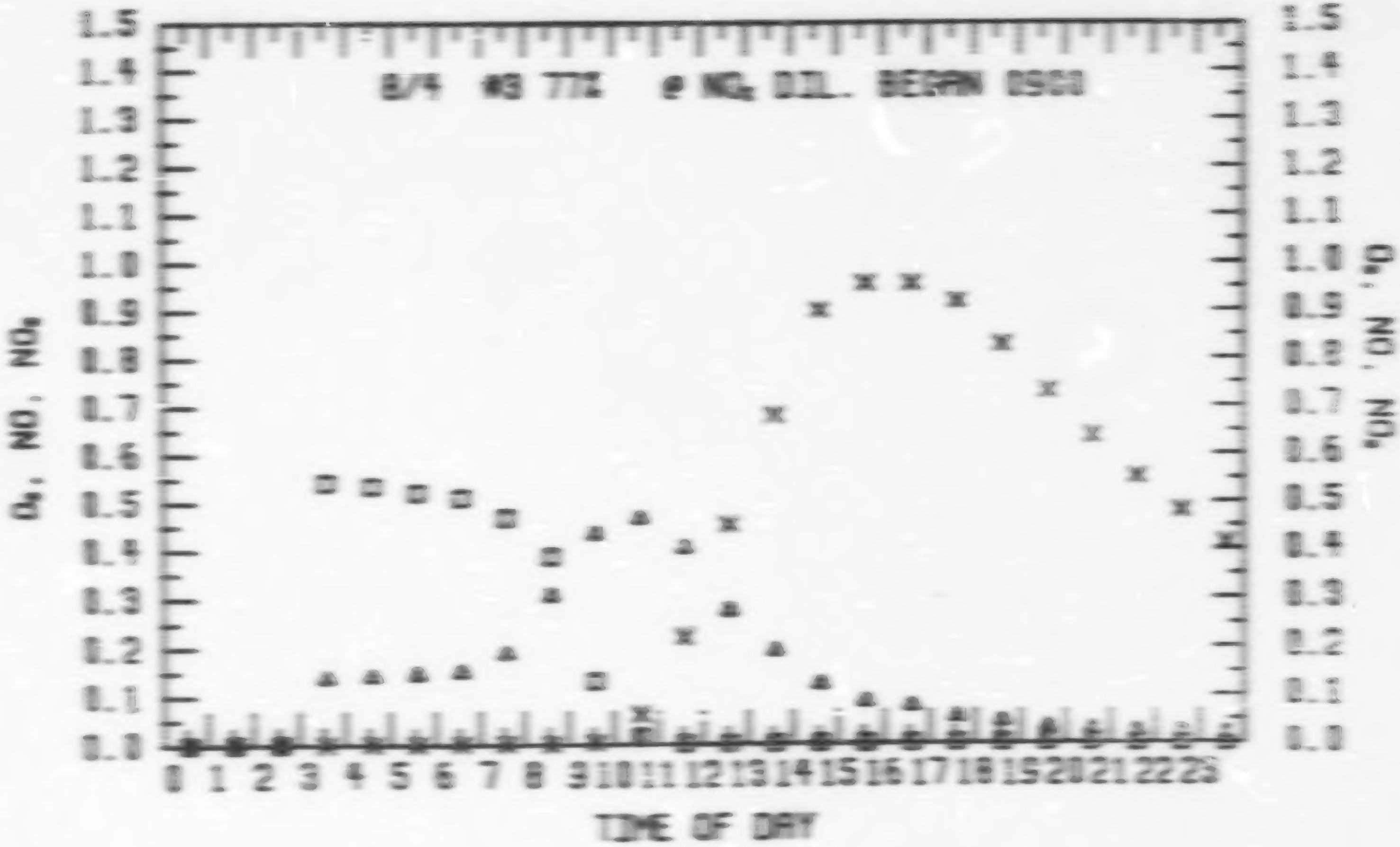

8/5 #2 77% @ NO₂ DIL. ENDED 0840
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

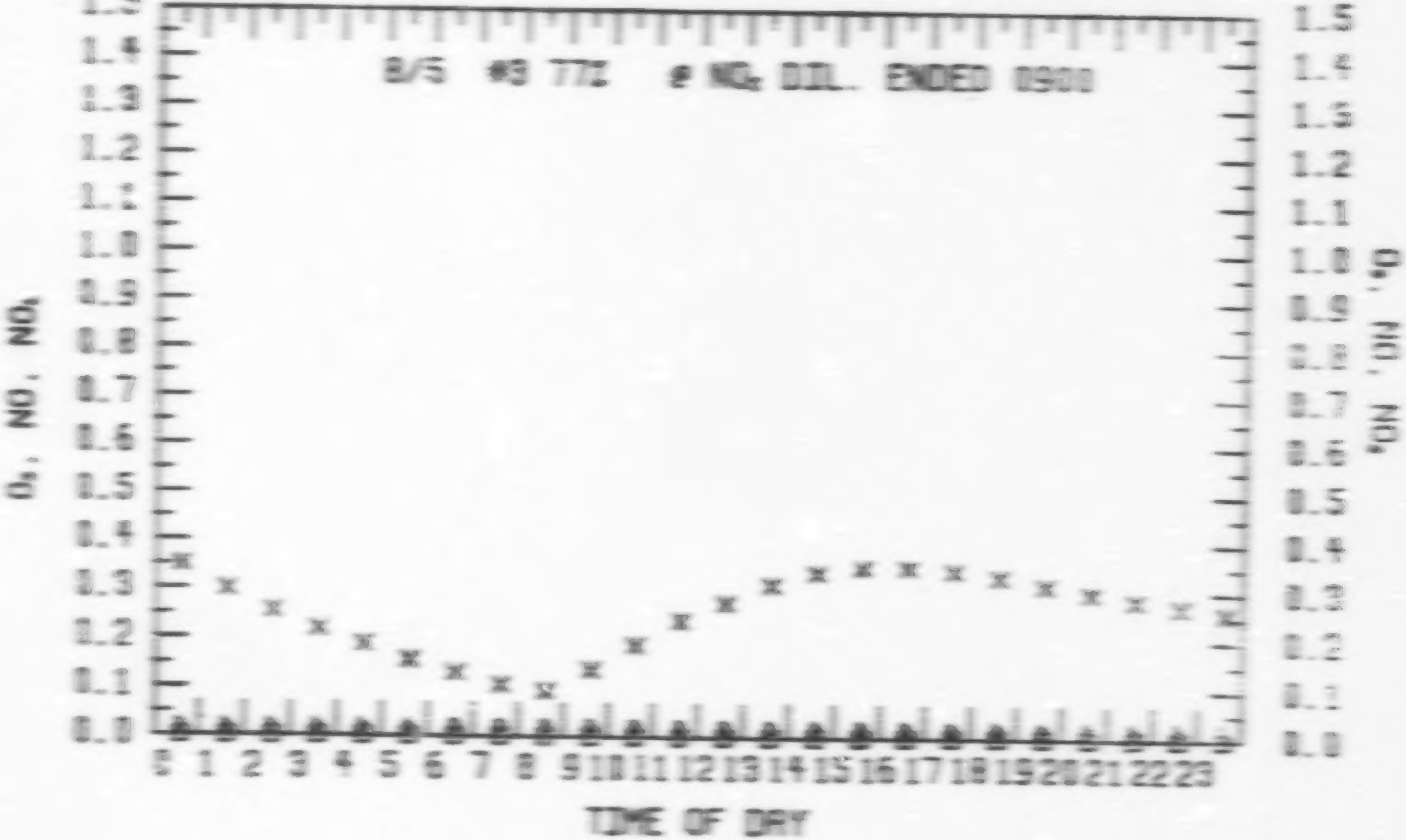

8/6 #2 77% @ NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

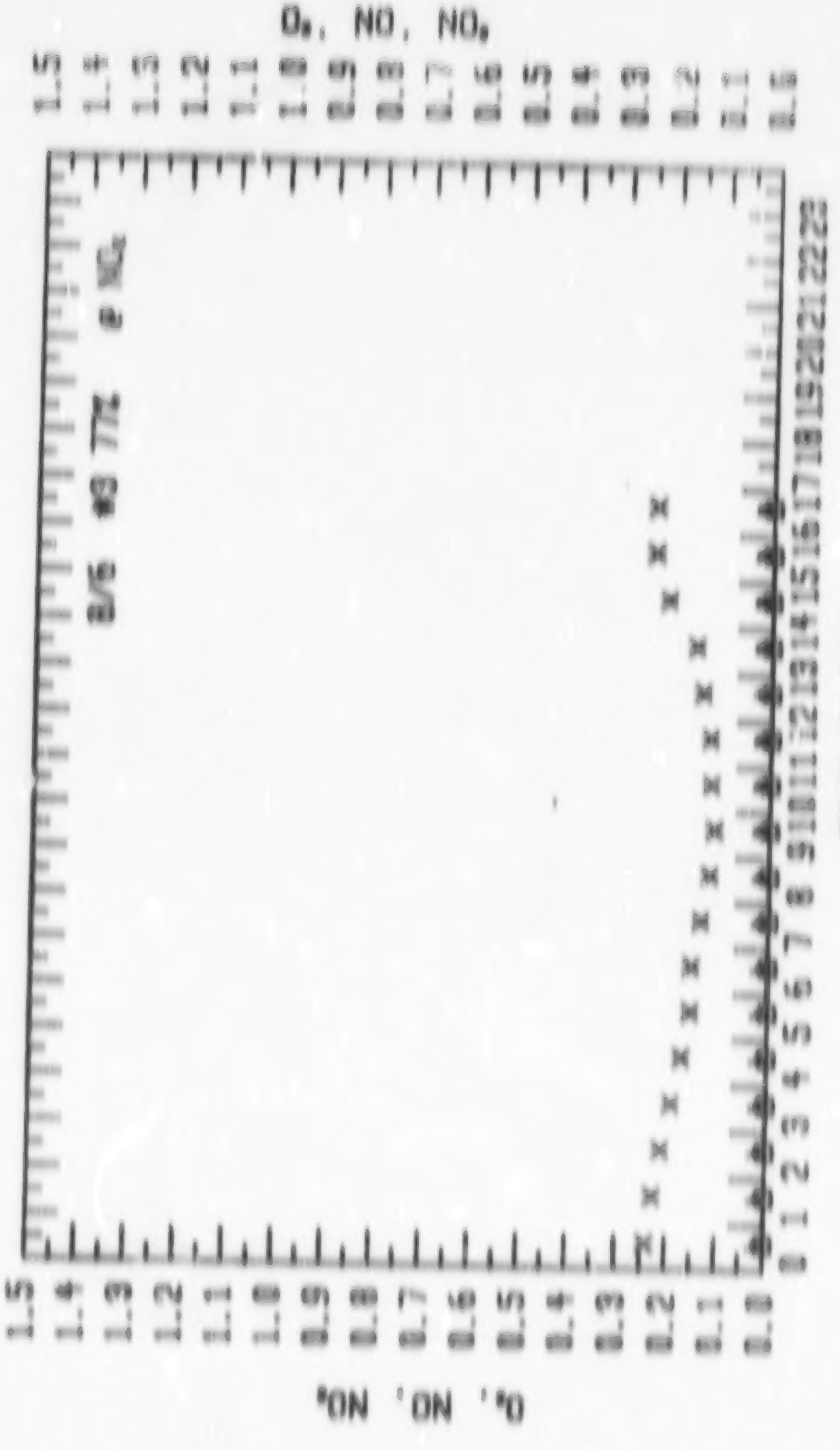

#2 8/4
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
13.5
12.0
11.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

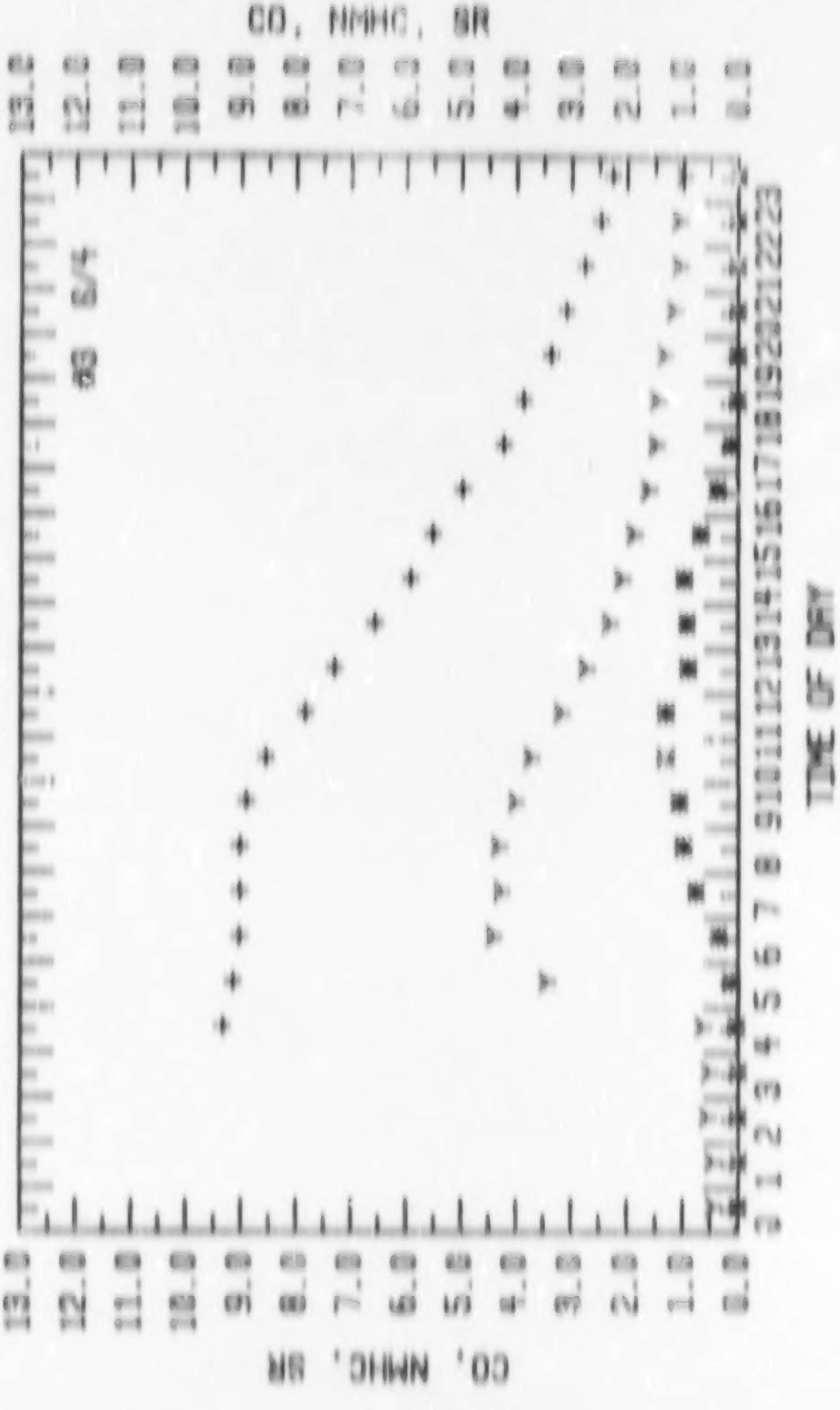

#2 8/5
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

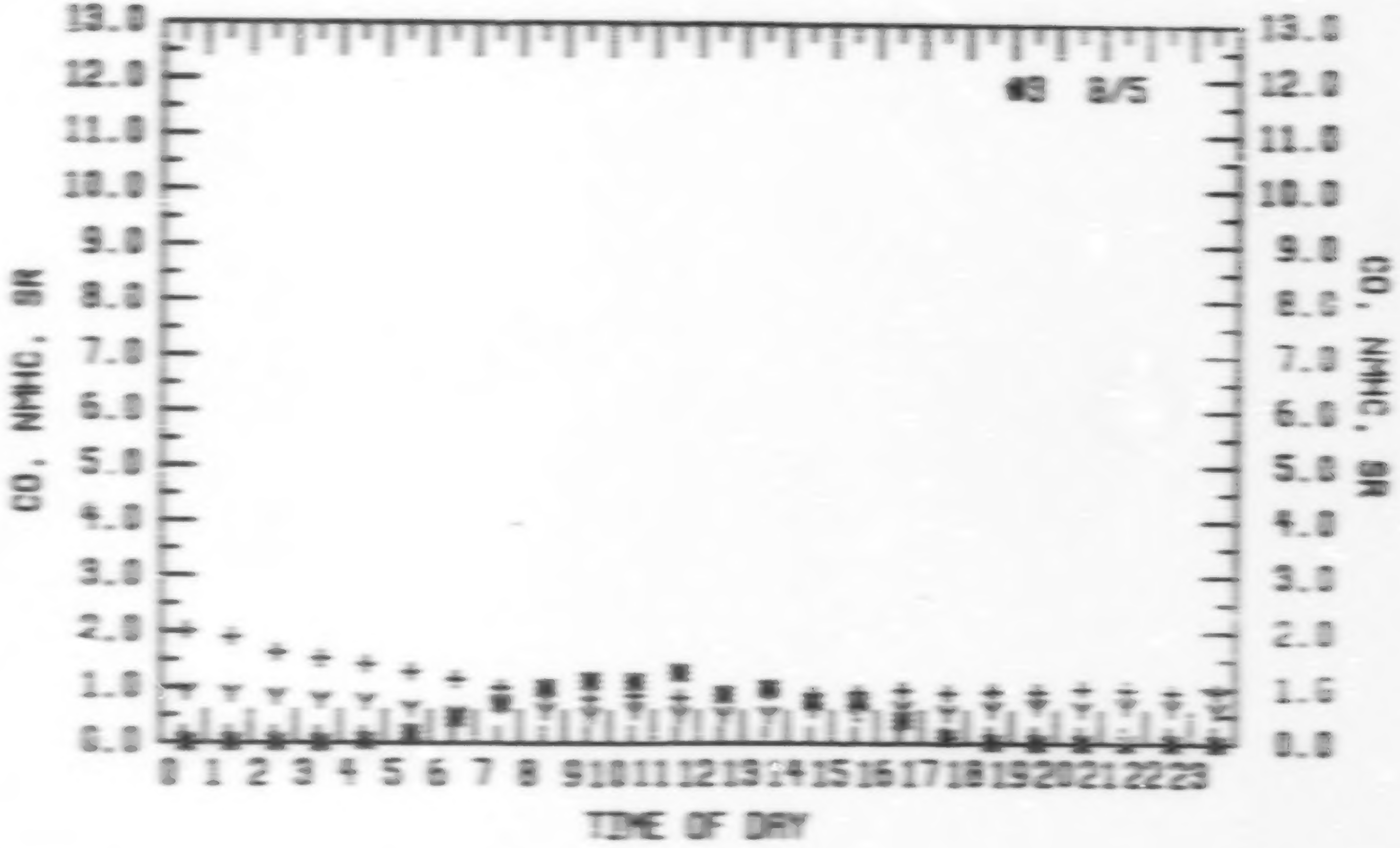

#2 5/5
CO, NMHC, SR
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

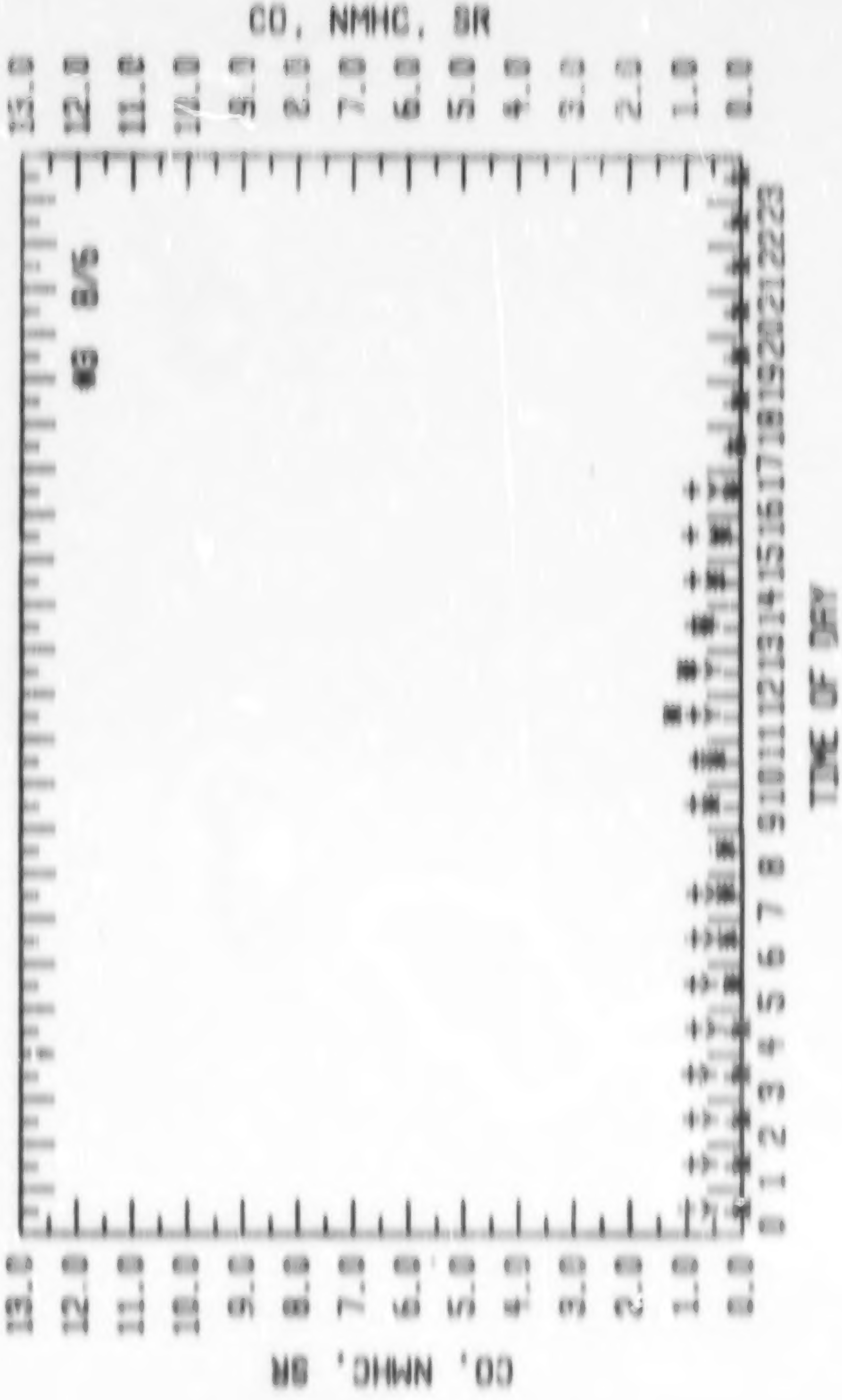

8/4 #3 77% @ NO₂ DIL. BEGAN 0900
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

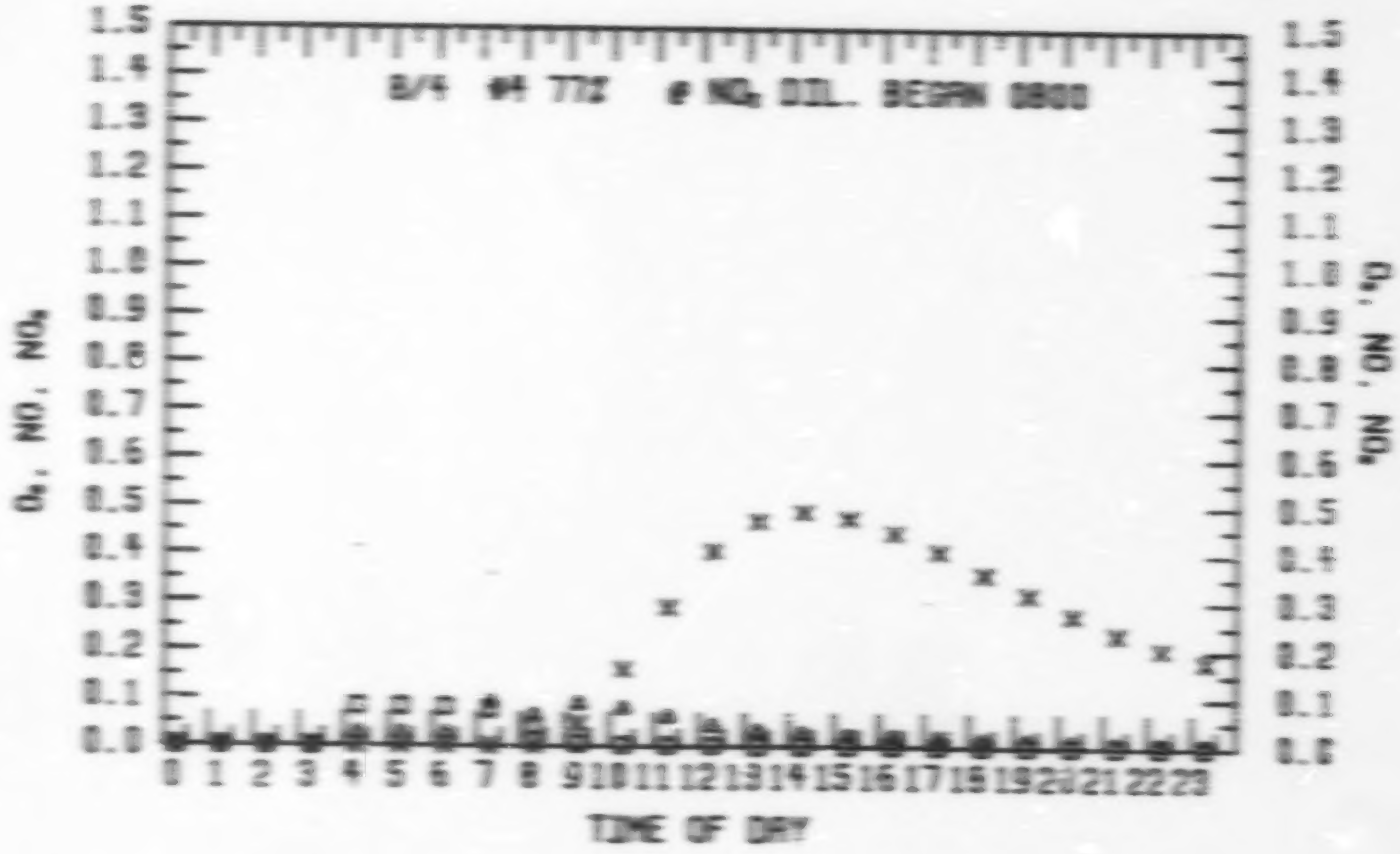

8/5 #3 77Z # NO₂ DIL. ENDED 0900
O₃, NO, NO₂
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

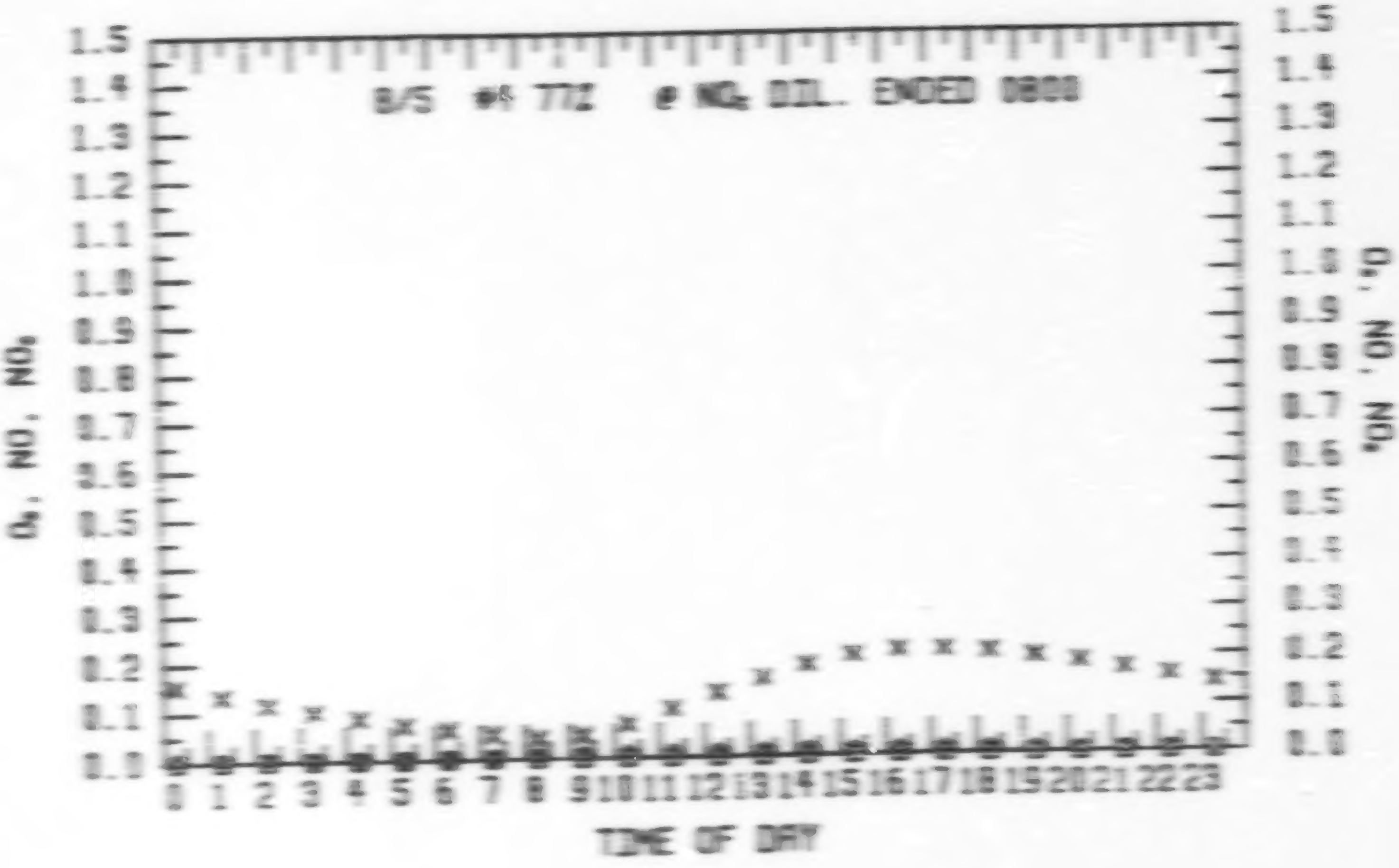

O3, NO, NO2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8/6 #3 77E # NOx
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
O3, NO, NO2

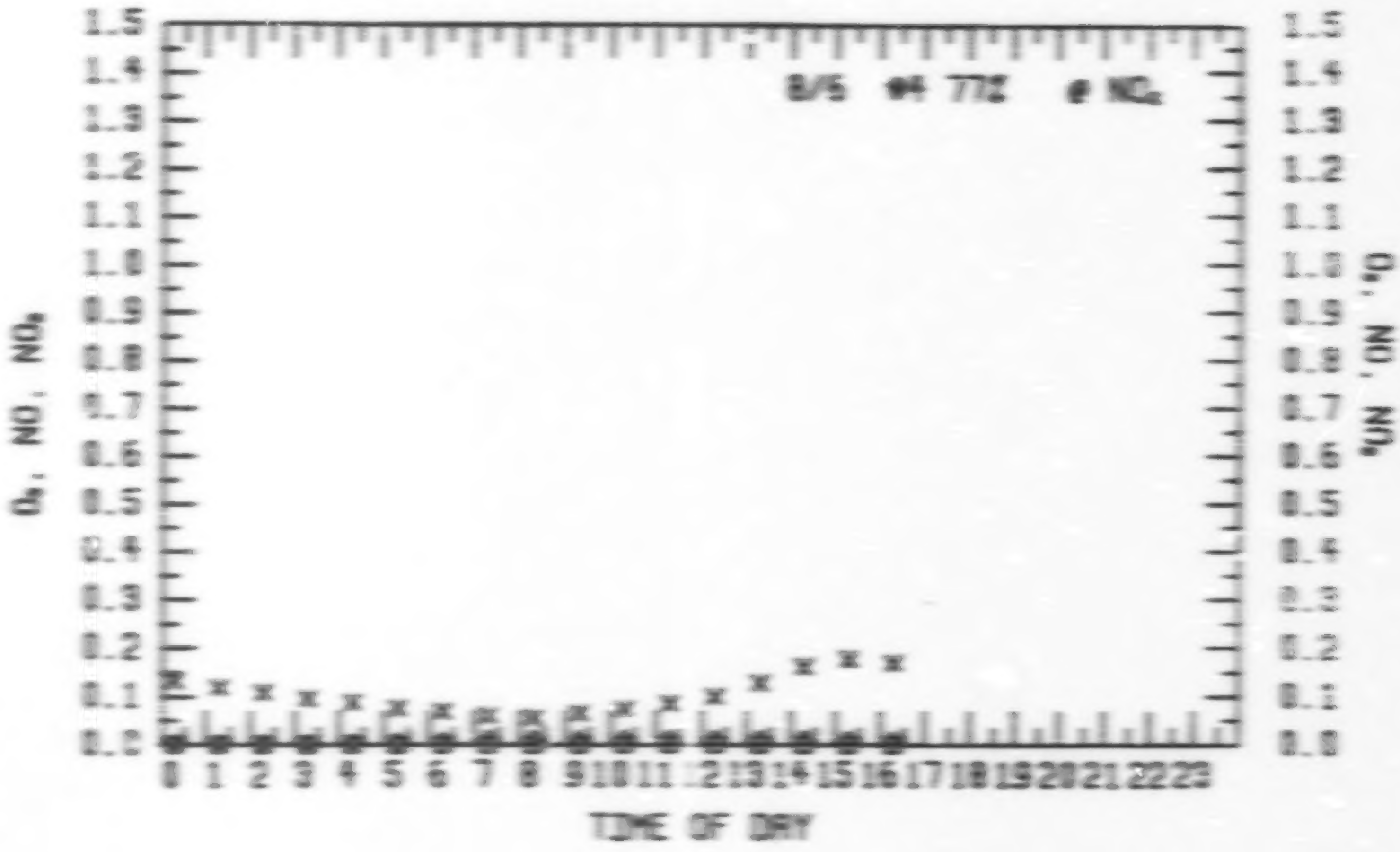

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#5 5/4
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

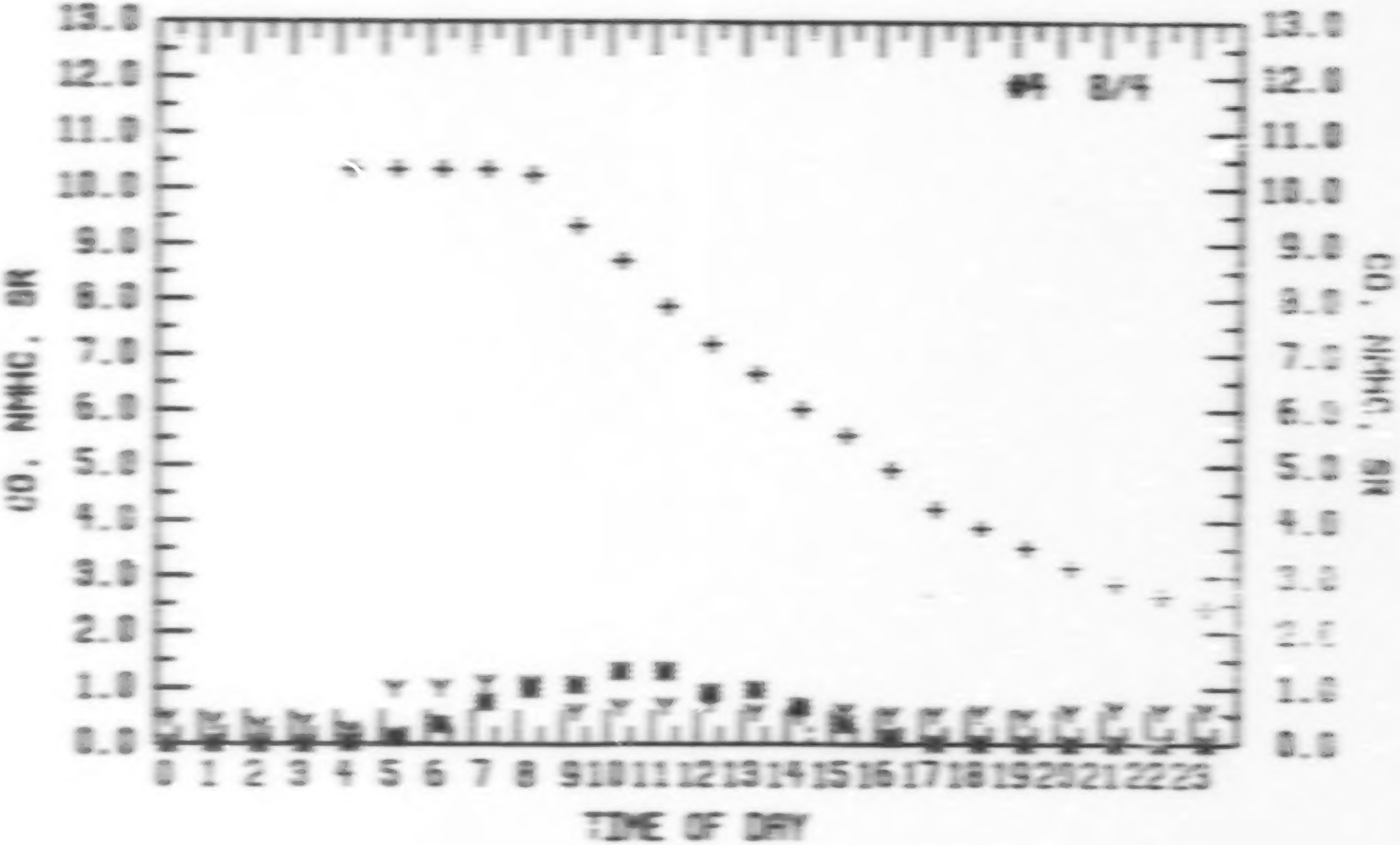

#3 8/5
CO, NMHC, SR
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

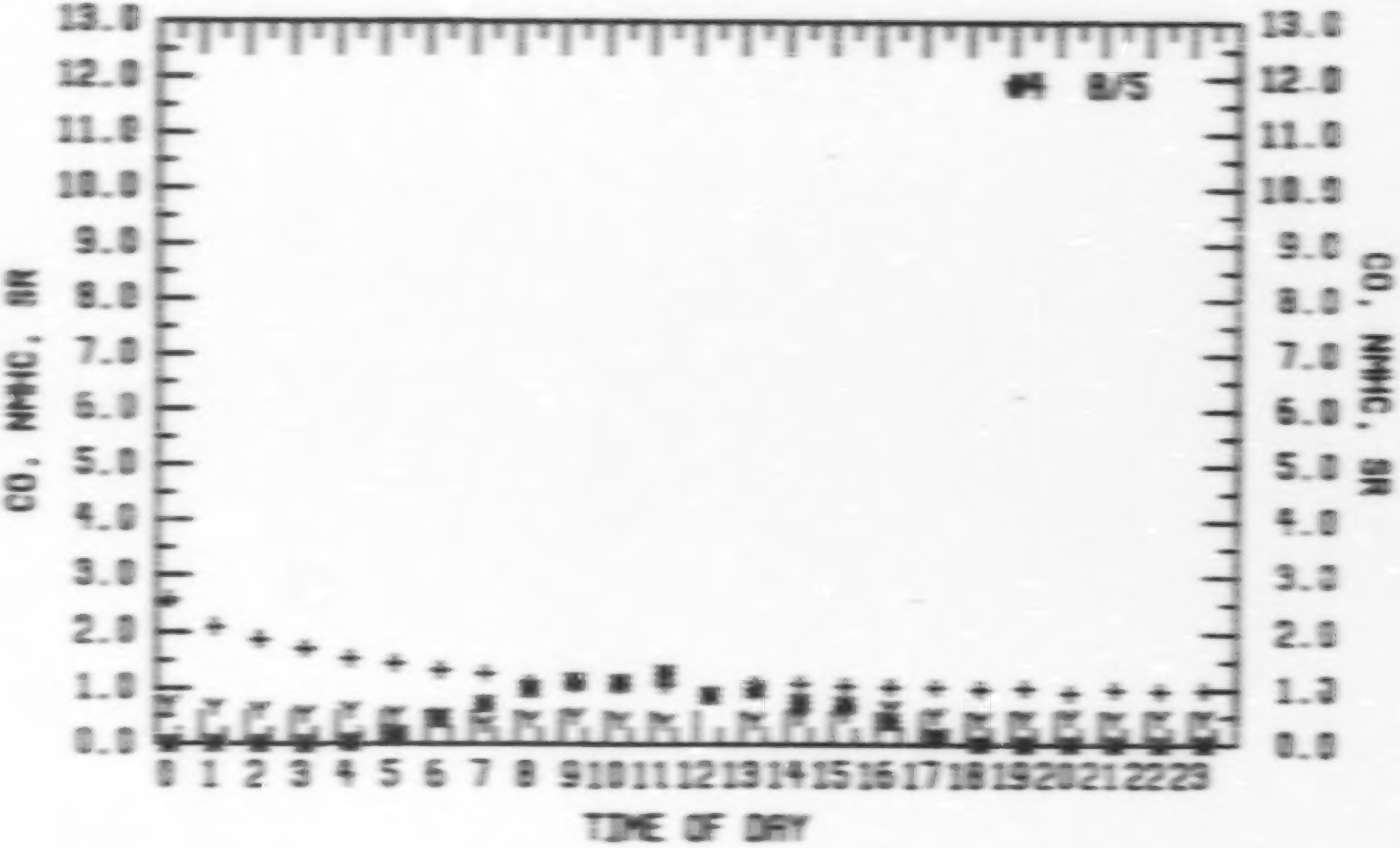

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
*G 8/5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

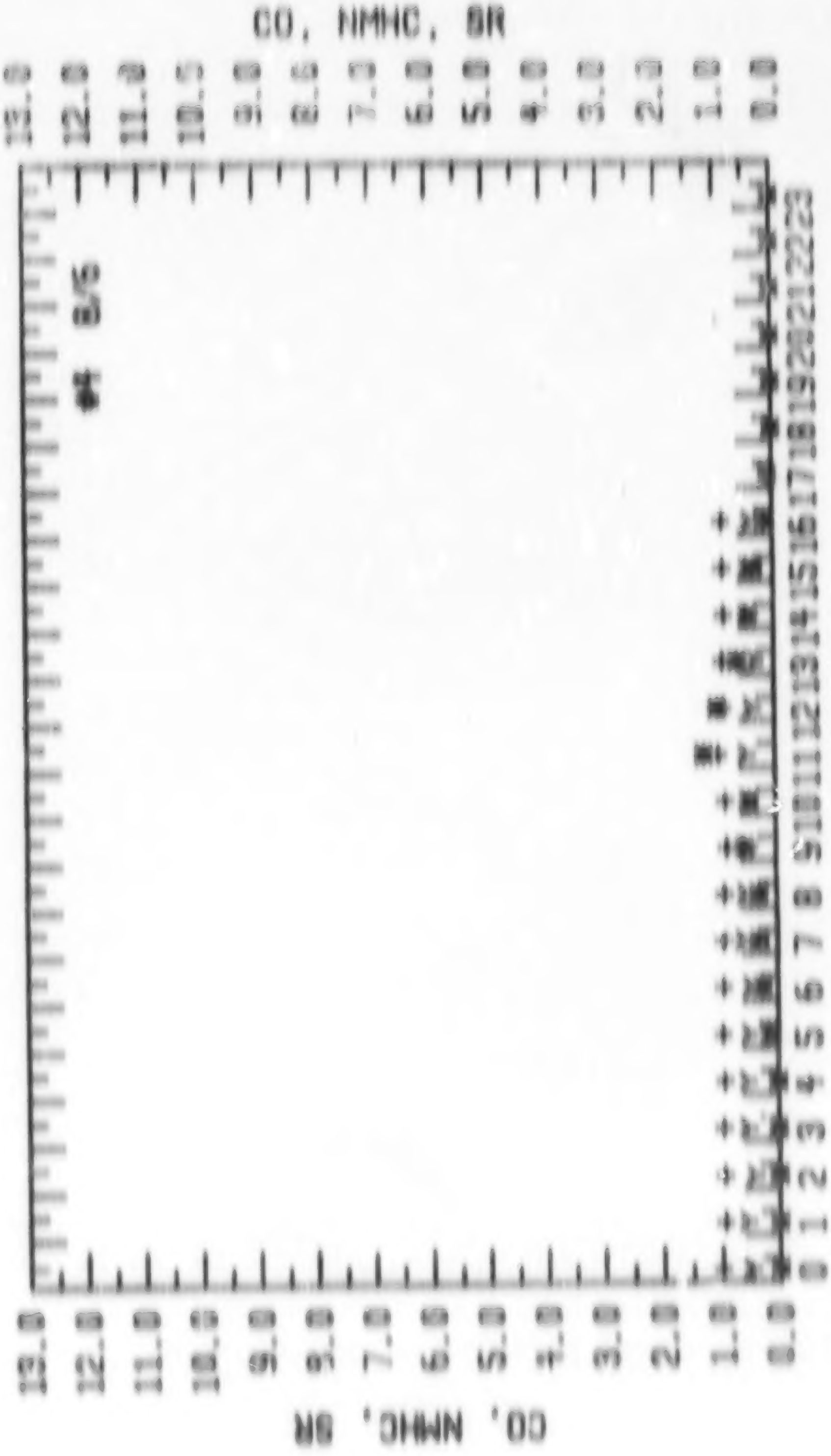

8/4 #4 77% # NO2 DIL. BEGAN 0800
O3, NO, NO2
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

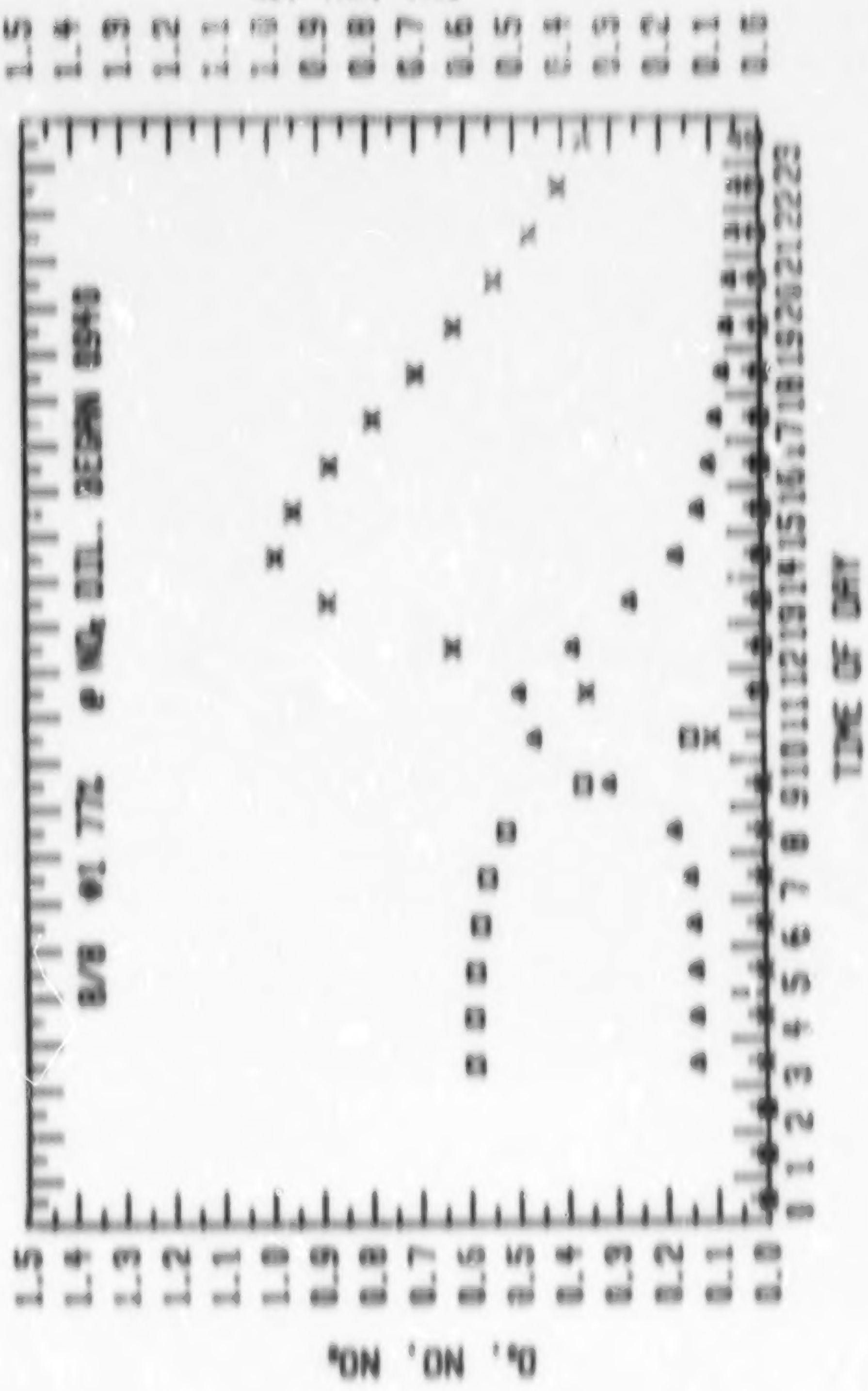

8/5 #4 77% @ NO2 DIL. ENDED 0800
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

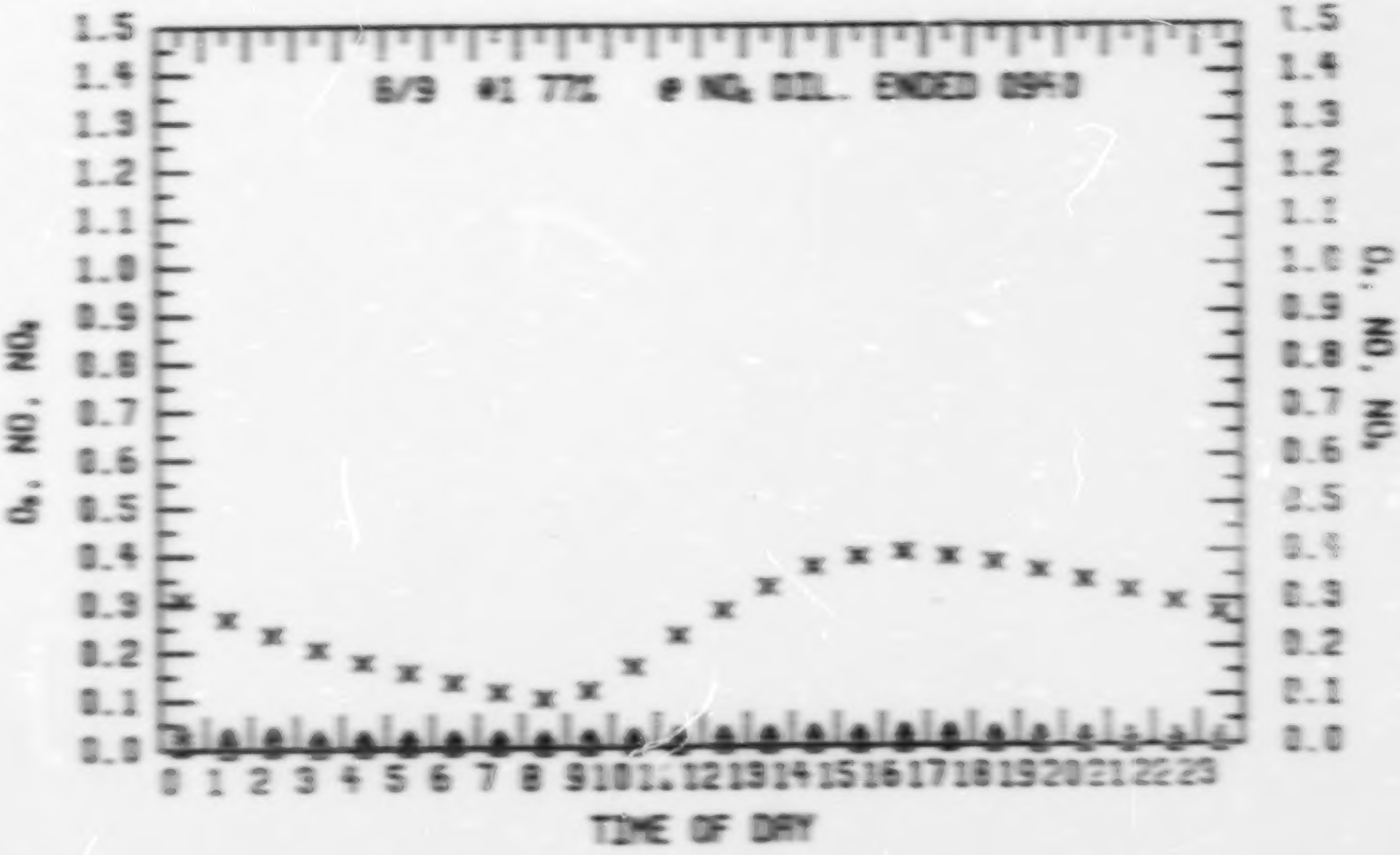

8/5 #4 77Z # NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

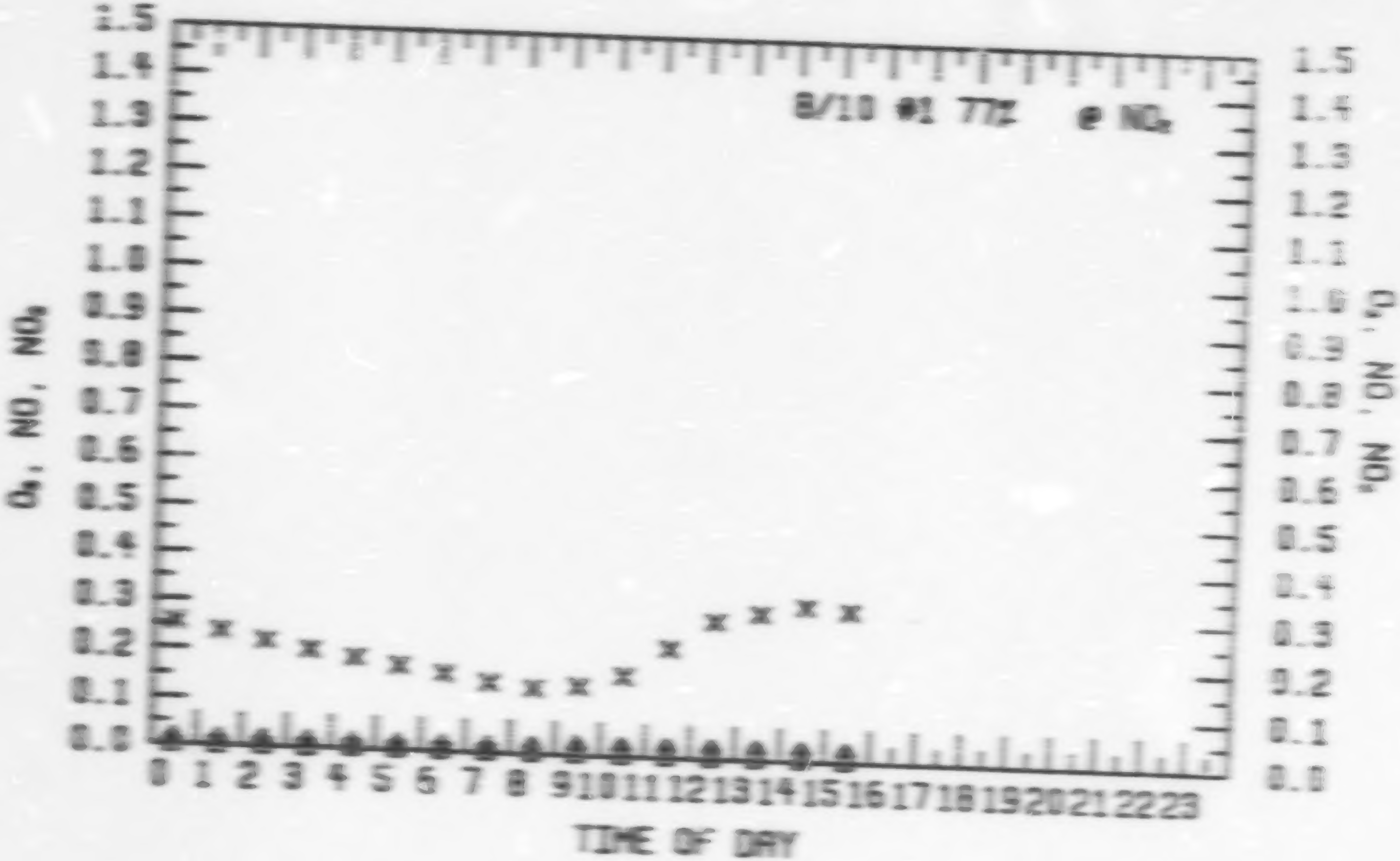

#4 8/4
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#4 8/5
CO, NMHC, SR
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

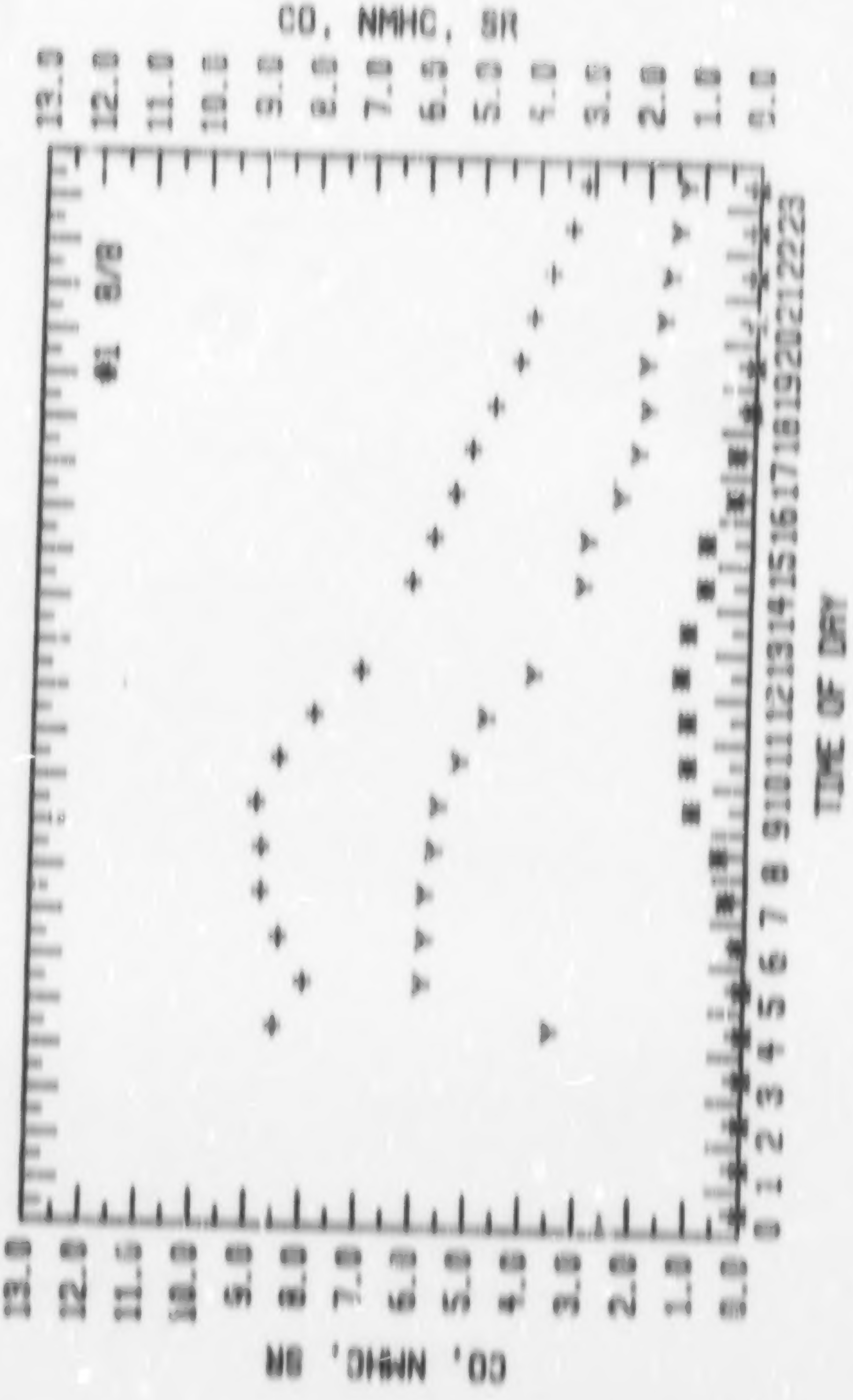

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#4 8/6
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR

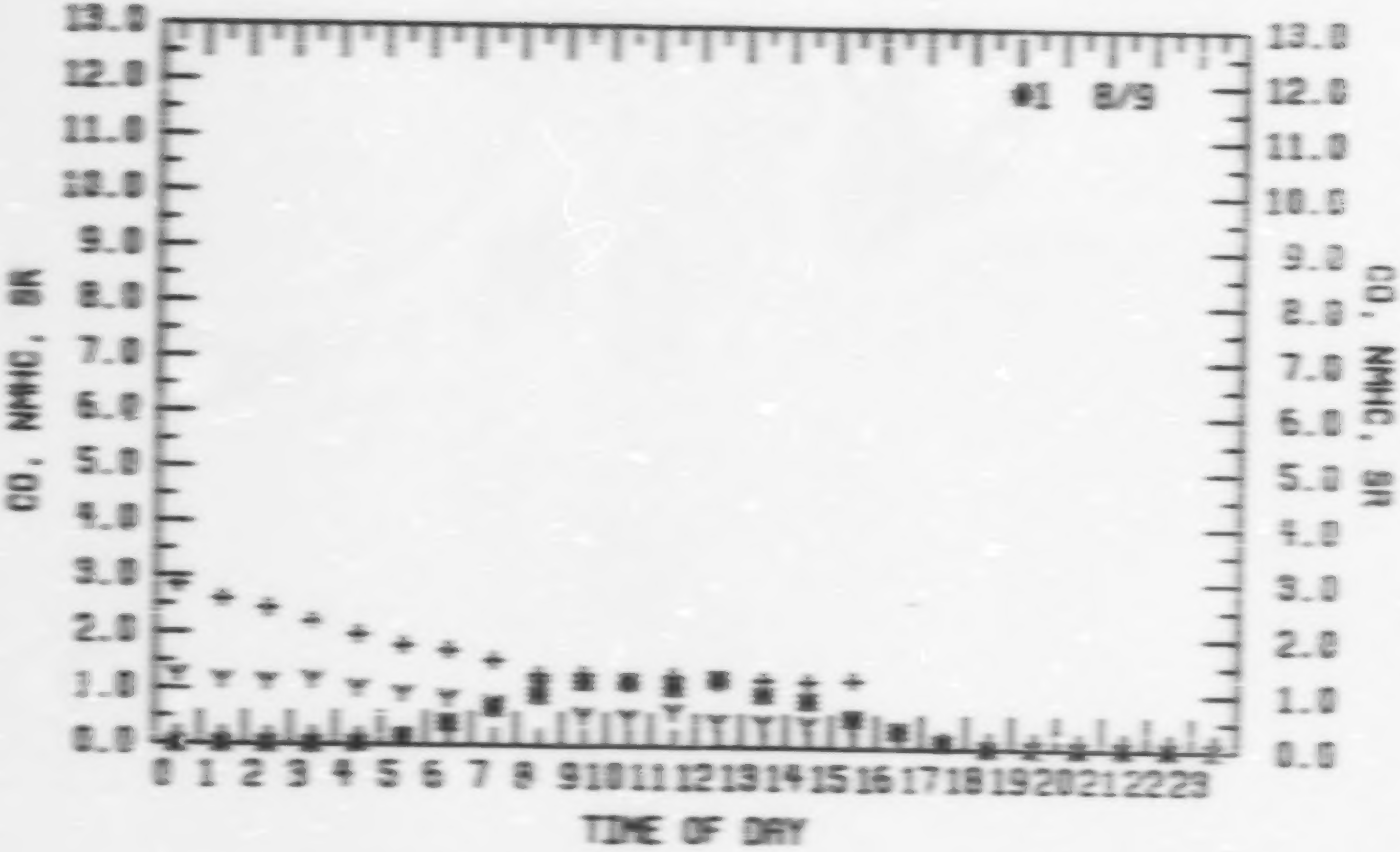

O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8/8 #1 77L @ NO₂ DIL. BEGAN 0940
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
O₃, NO, NO₂

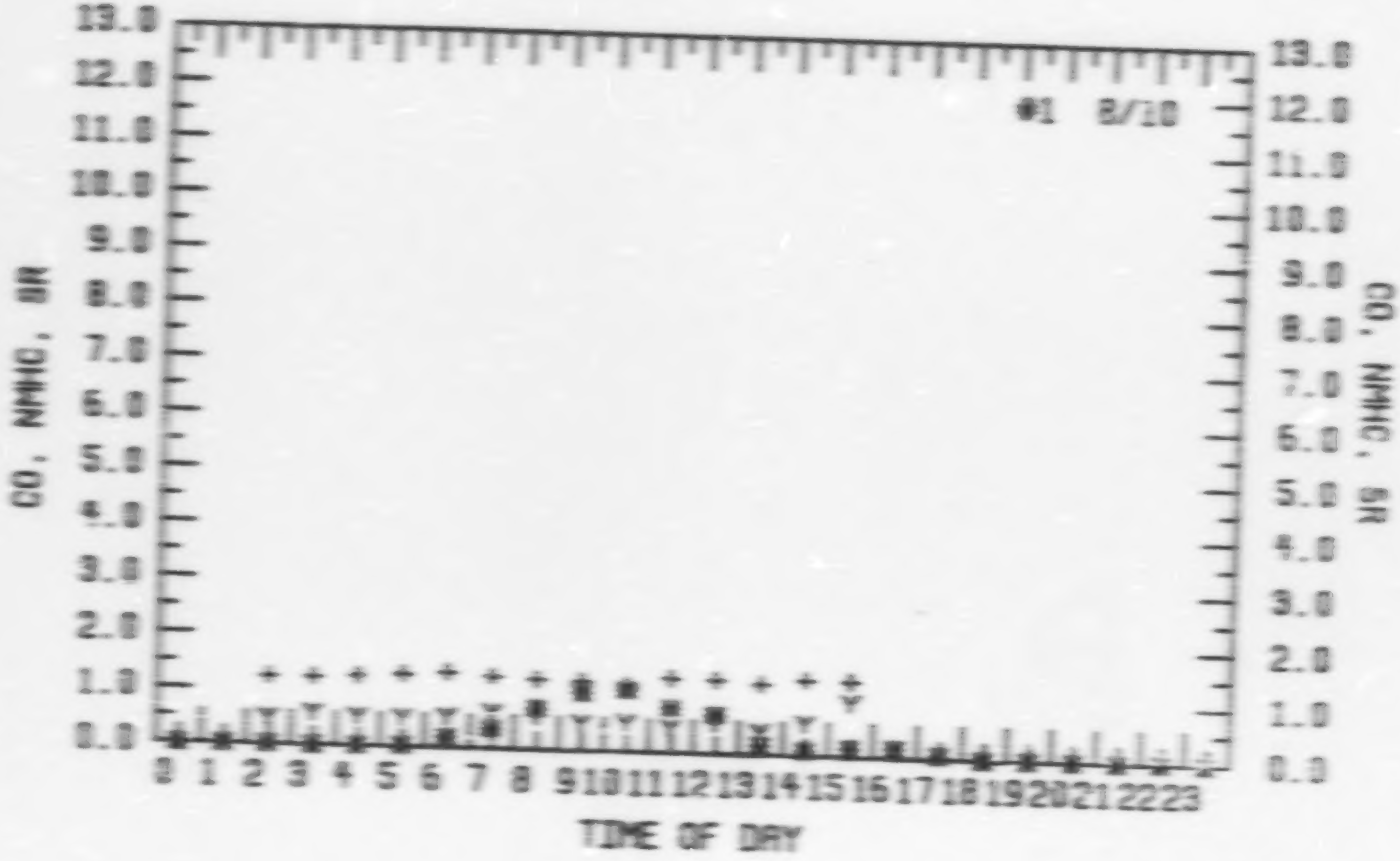

8/9 #1 77% @ NO_2 DIL. ENDED 0940
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
O_3, NO, NO_2

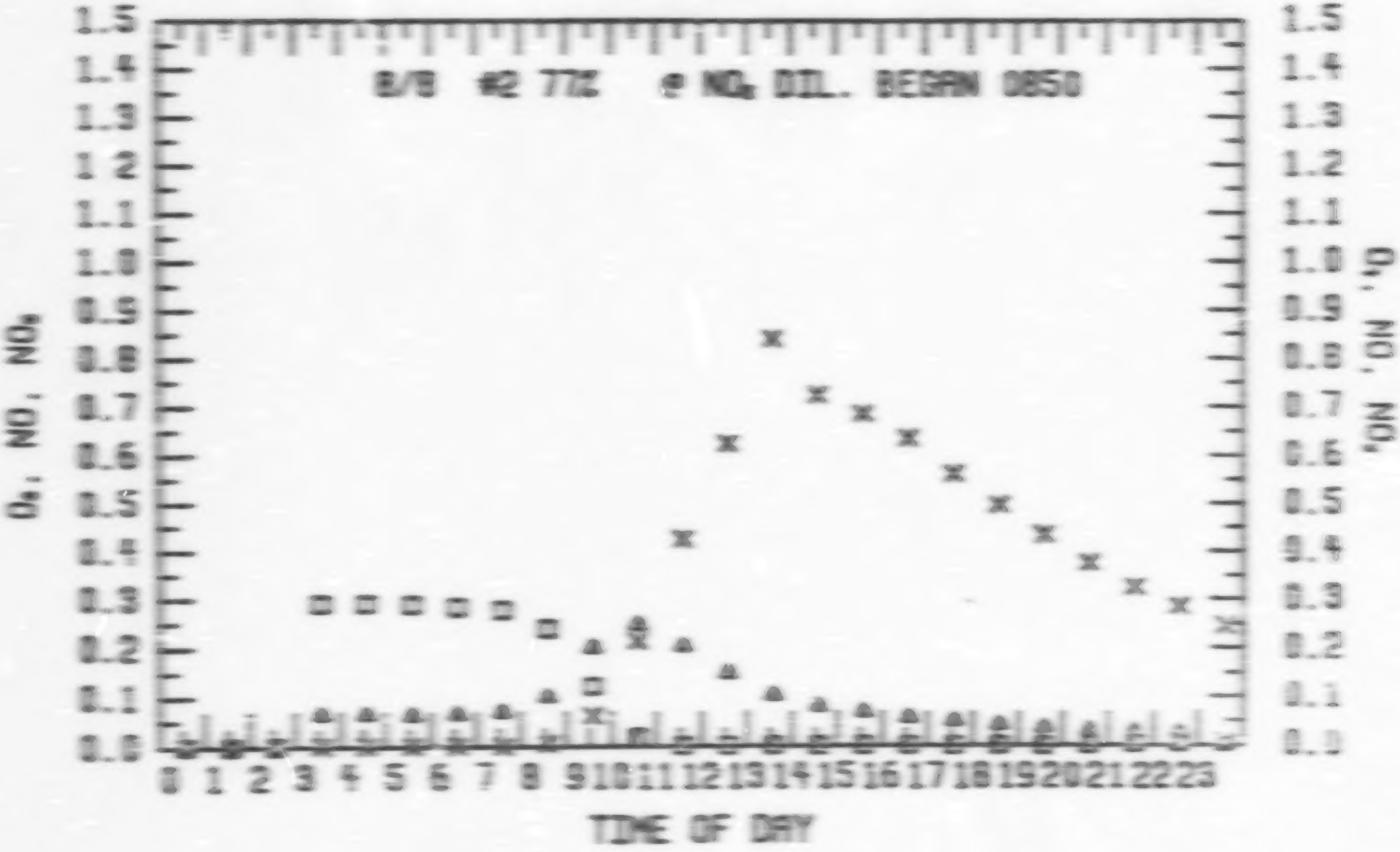


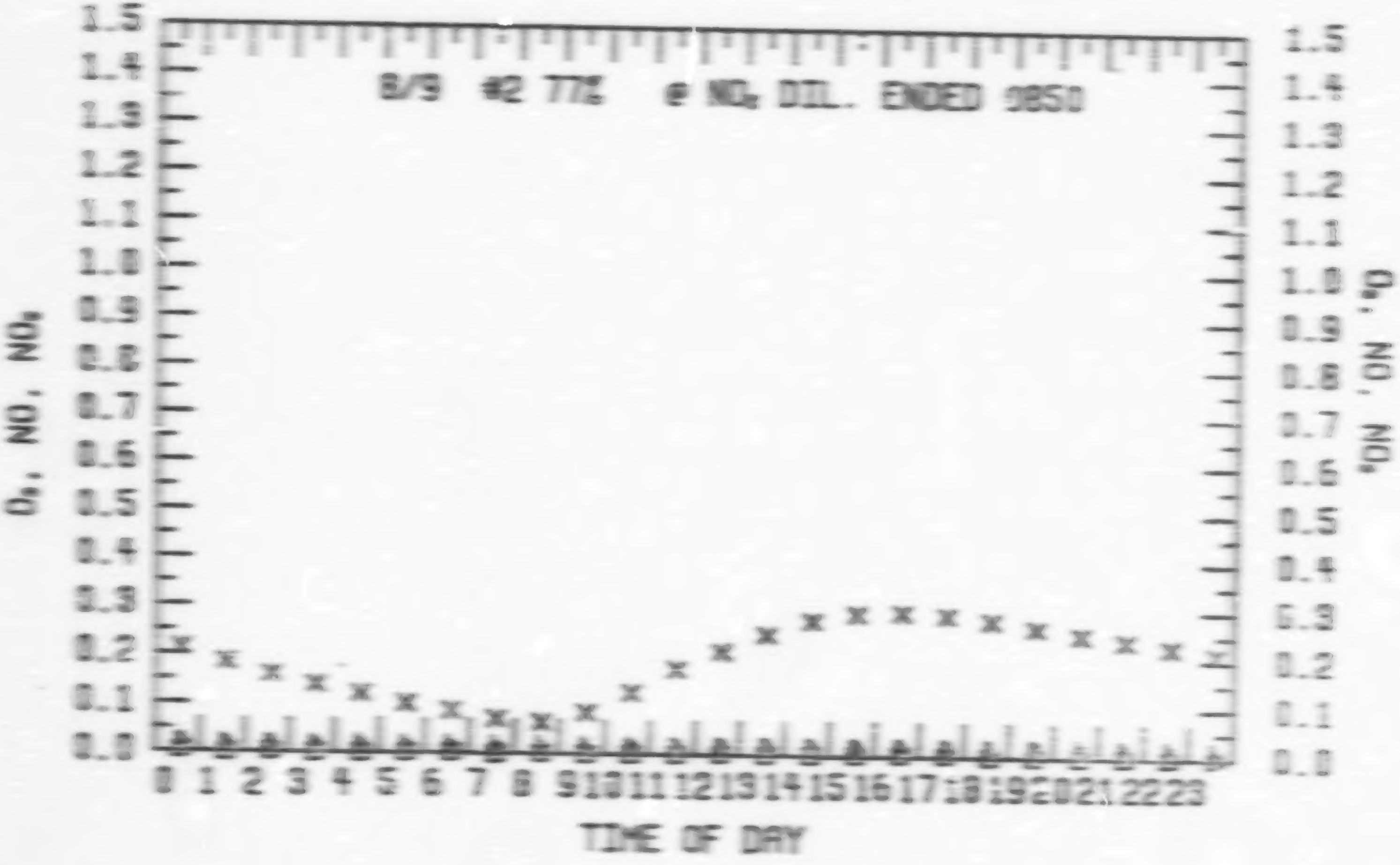
8/10 #1 77Z
@ NO2
O3, NO, NO2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

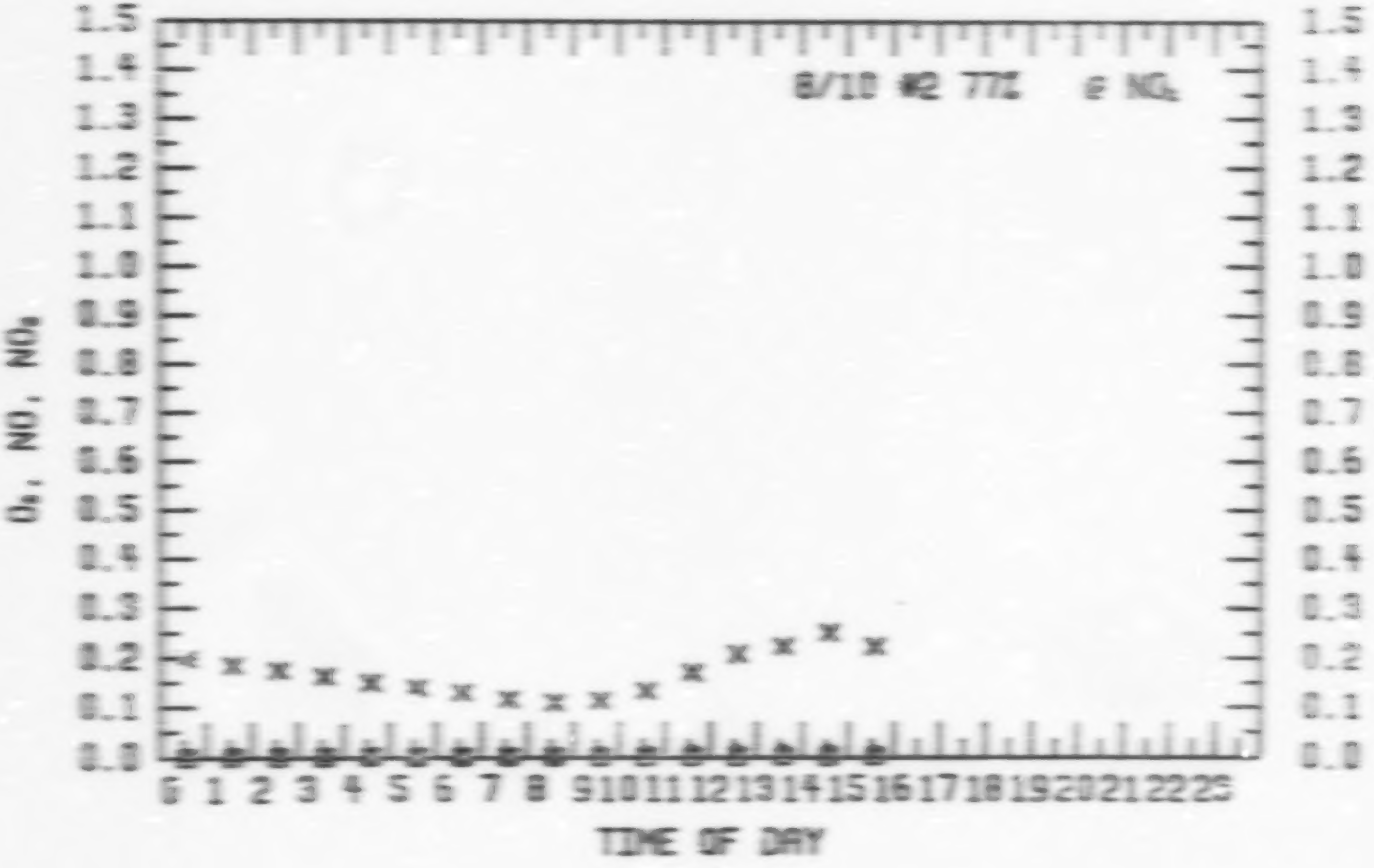

CO, NMHC, SR
13.5
12.0
11.0
10.5
9.0
8.0
7.0
6.5
5.0
4.0
3.5
2.0
1.5
0.0
#1 8/8
13.0
12.0
11.5
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

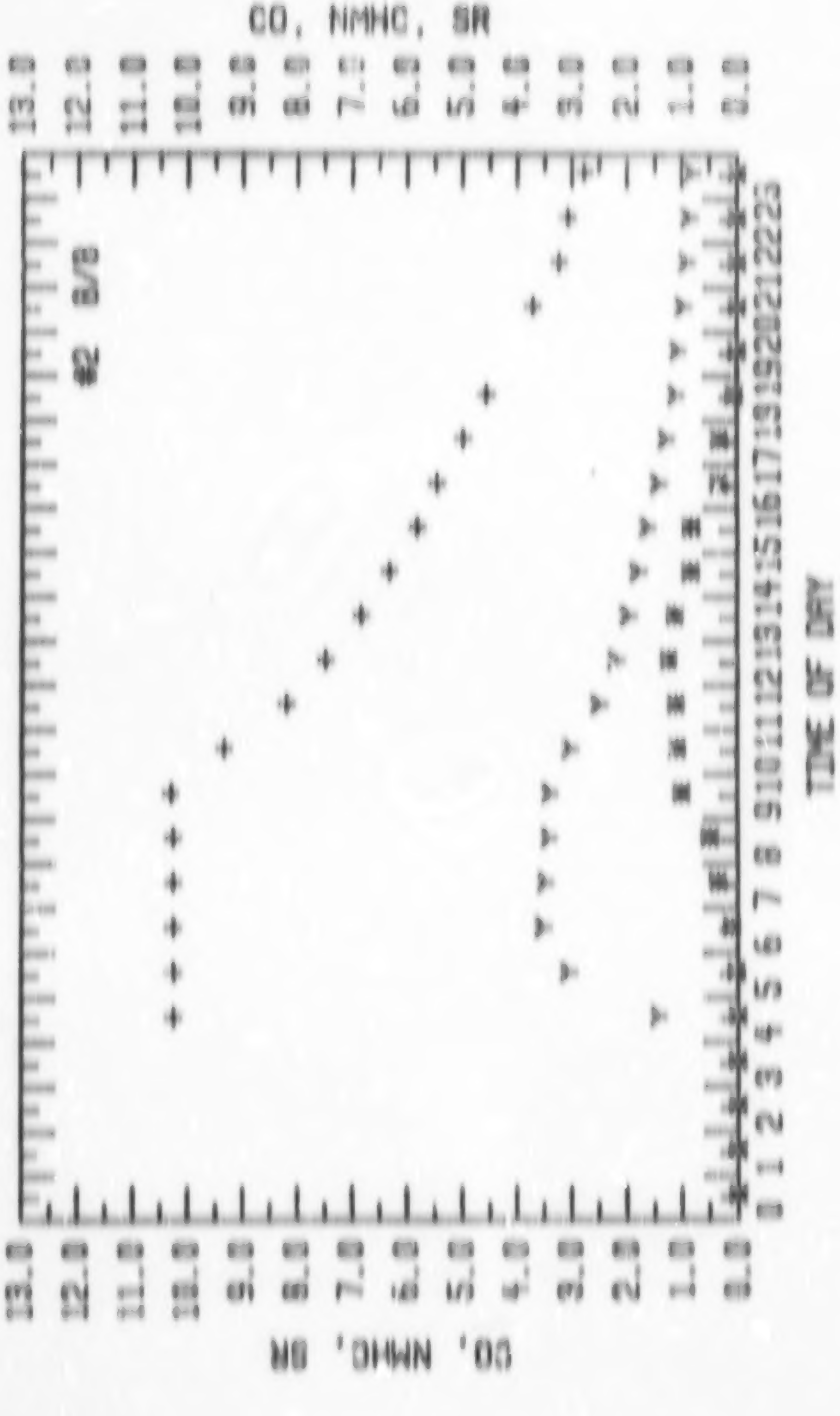

13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CO, NMHC, SR
#1 8/9
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#1 8/10
CO, NMHC, SR
CO, NMHC, SR
TIME OF DAY
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

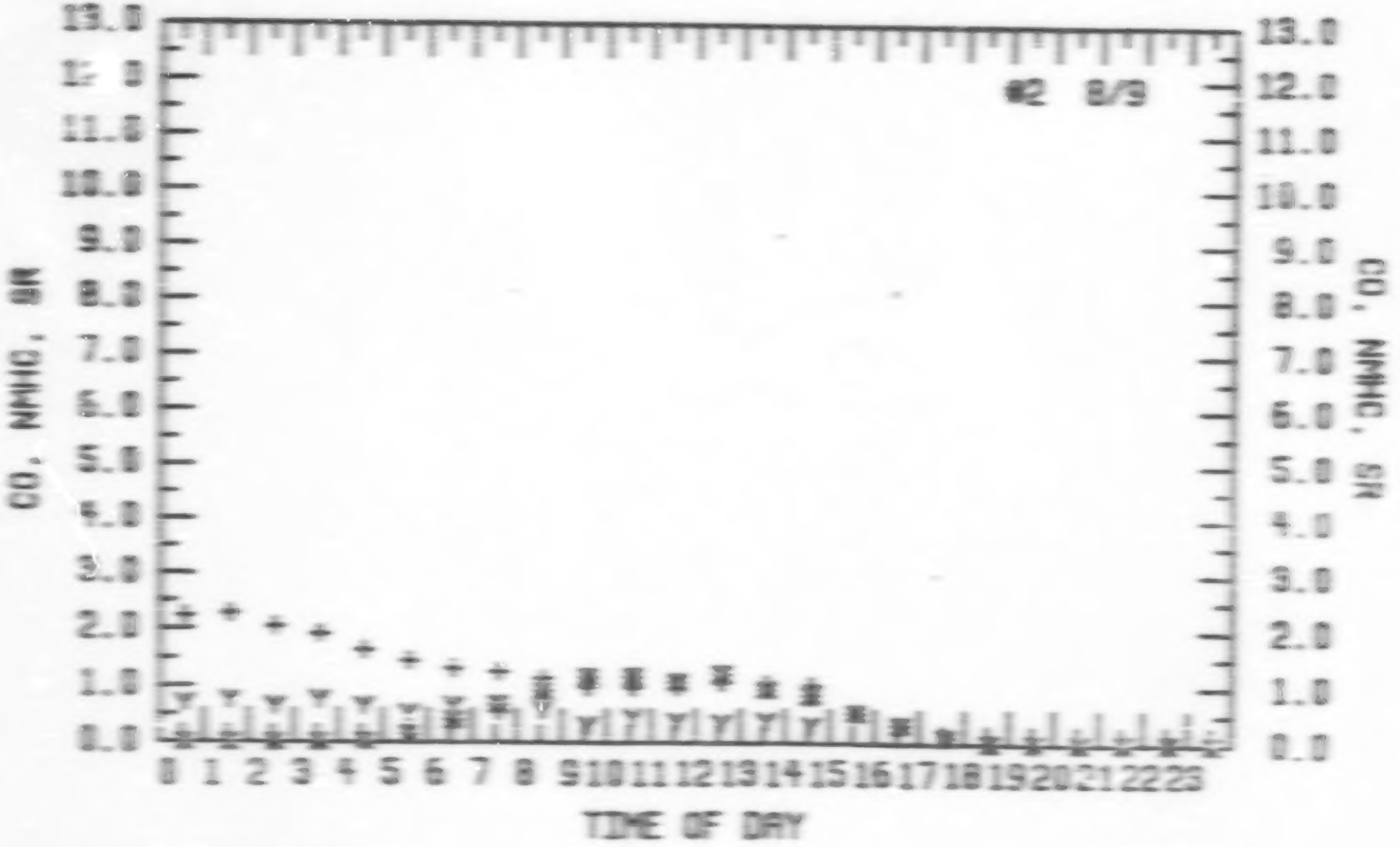

8/8 #2 77% @ NO₂ DIL. BEGAN 0850
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

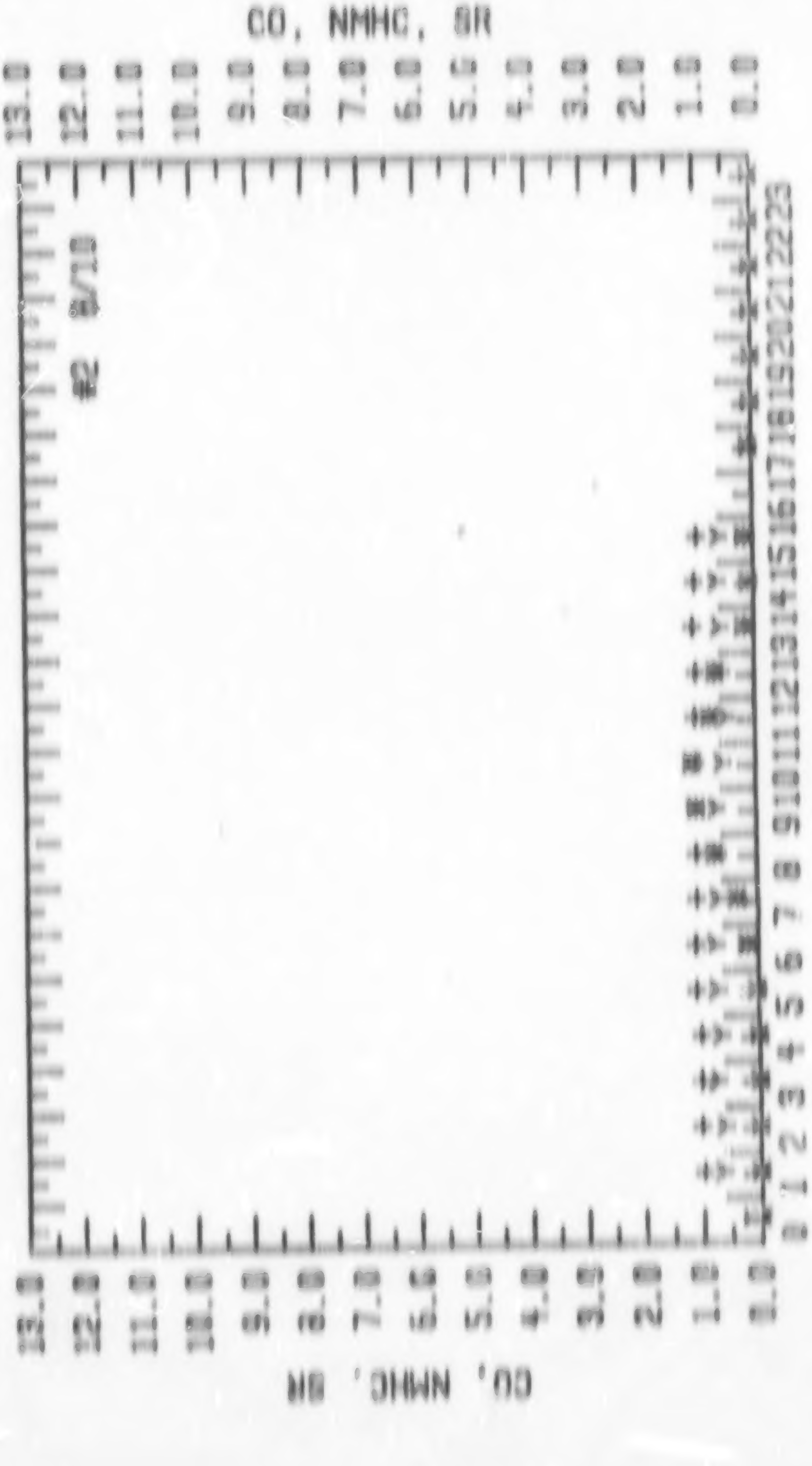

8/9 #2 77% @ NO₂ DIL. ENDED 0850
O₃, NO, NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

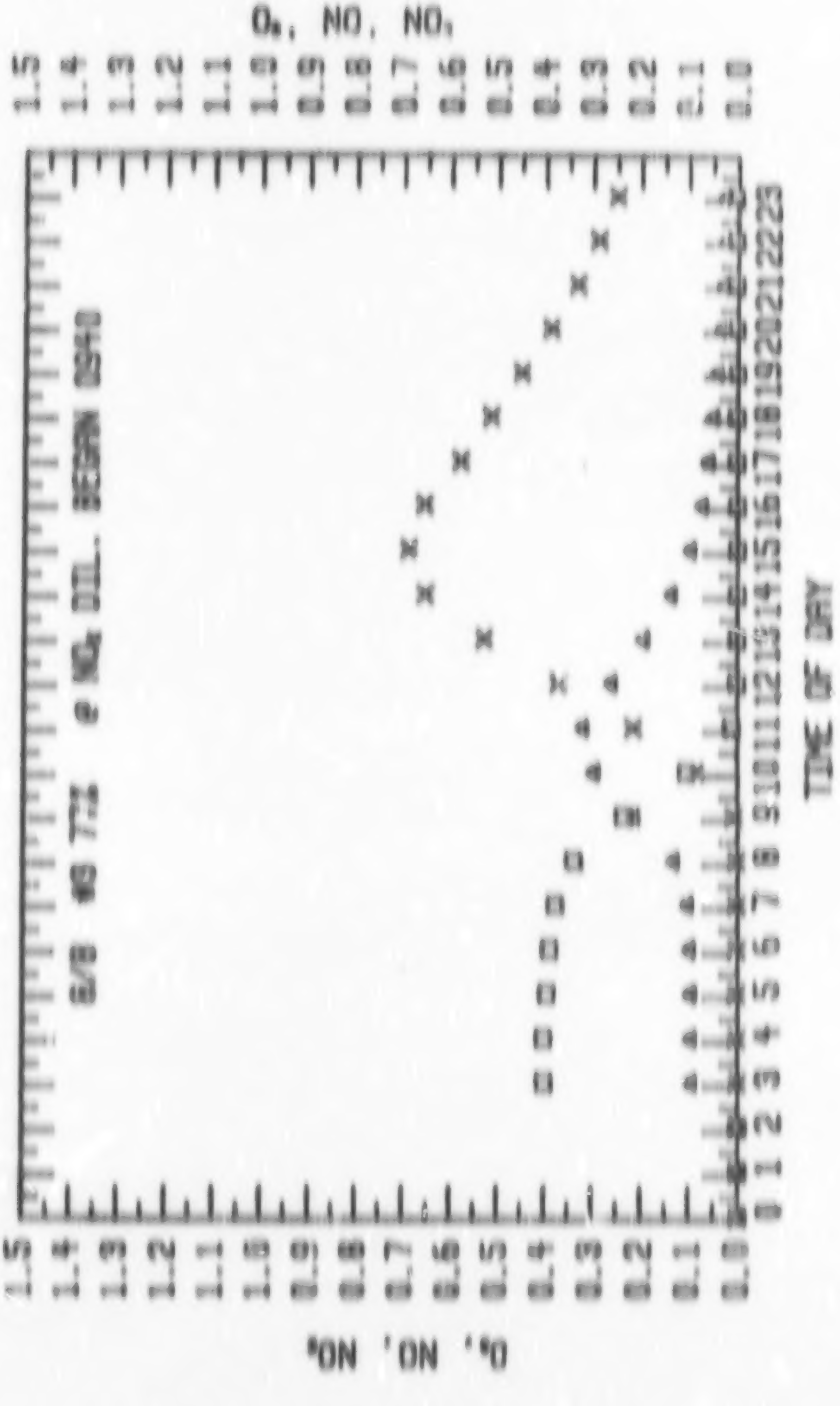

8/10 #2 77% ø NO₂
O₃, NO, NO₂
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

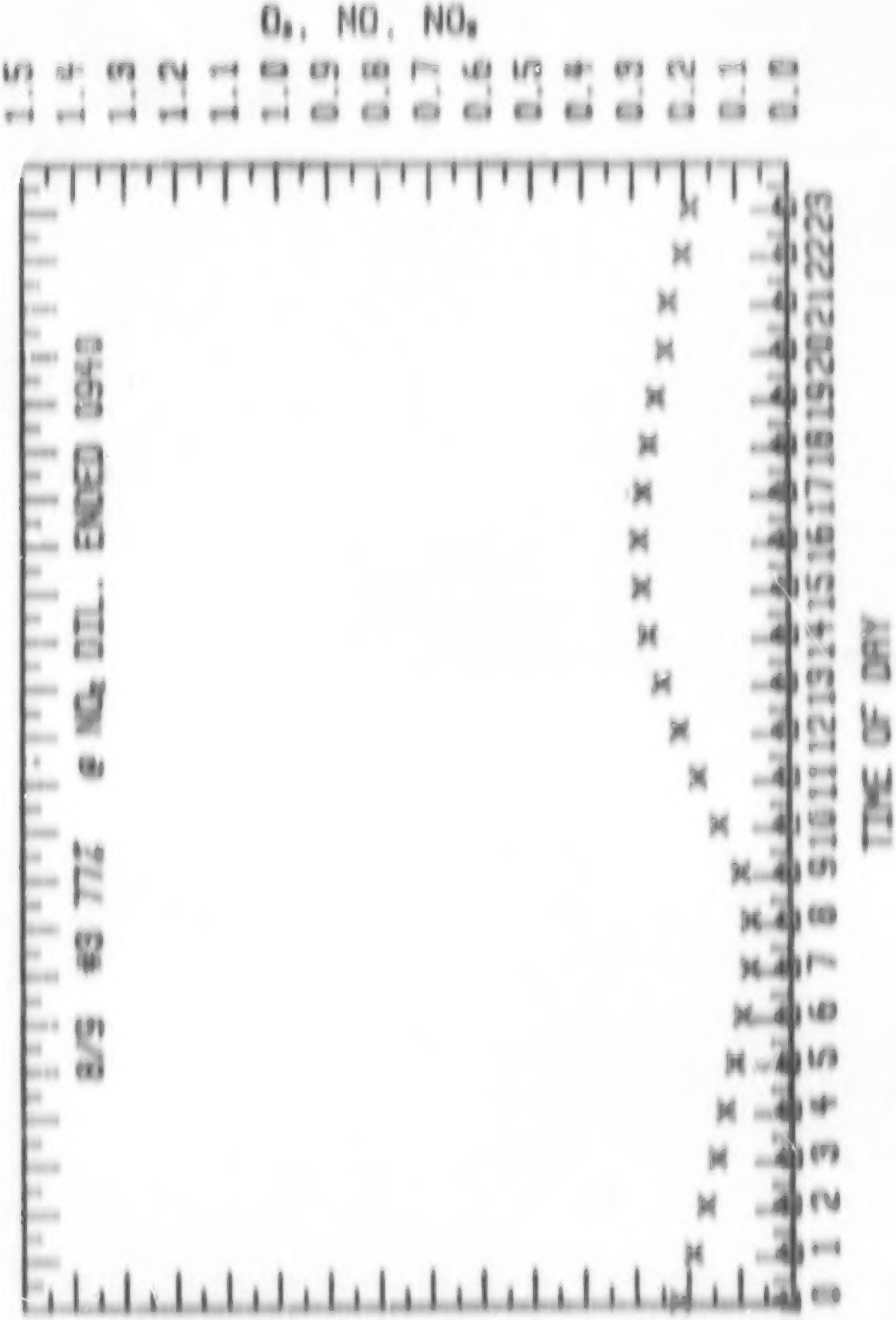


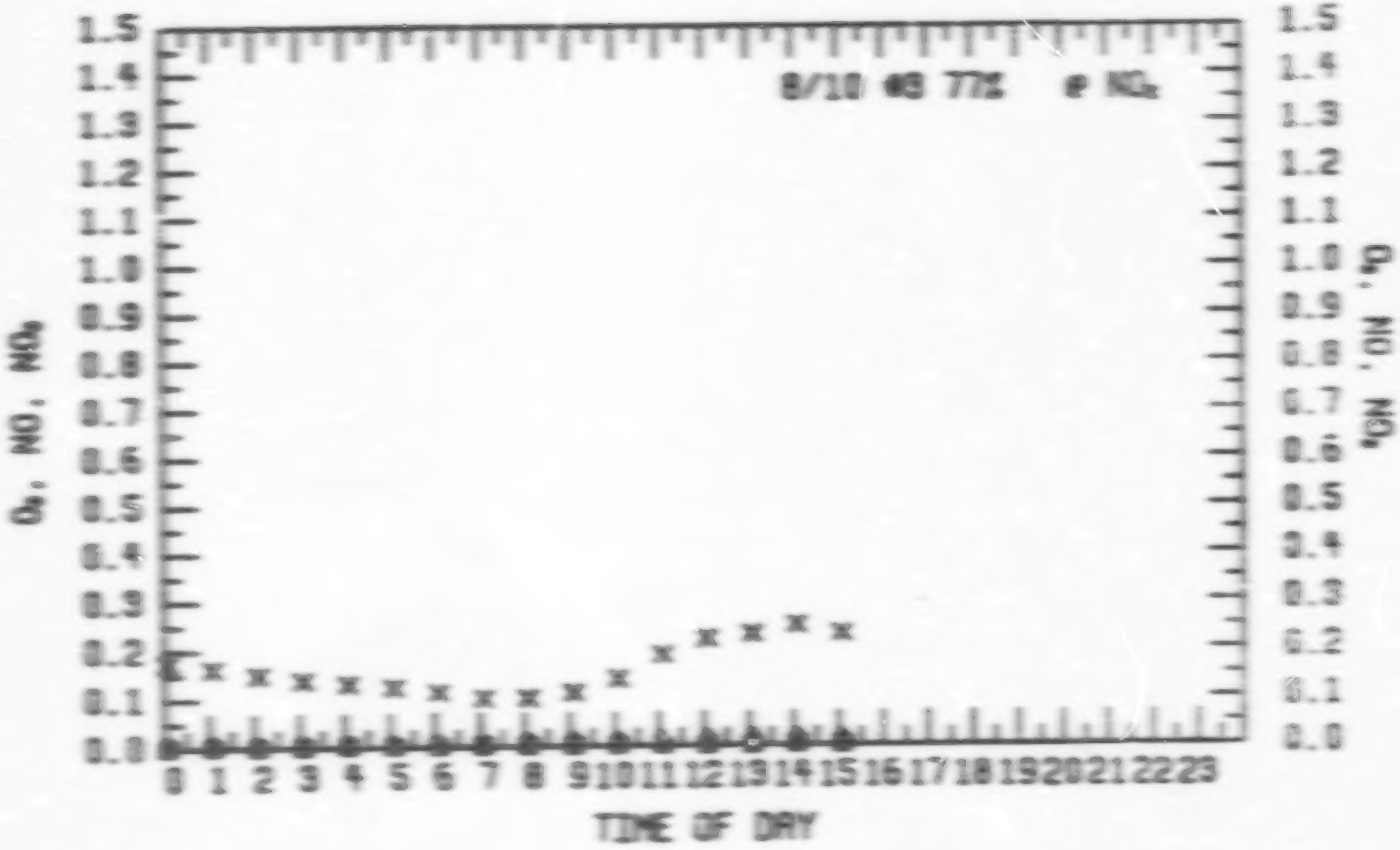
CO, NMHC, SR
#2 8/8
TIME OF DAY
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

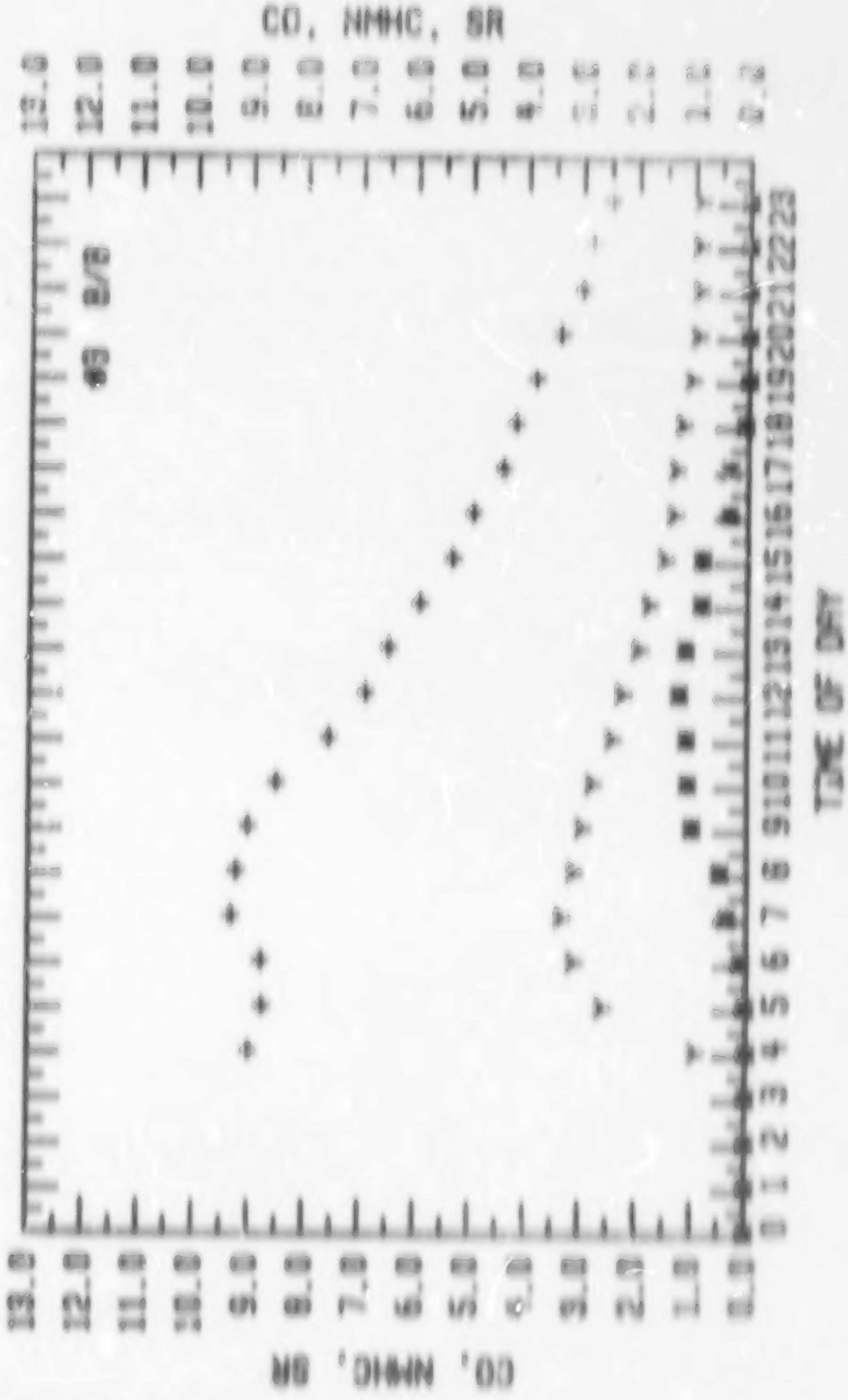

#2 8/9
CO, NMHC, SR
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

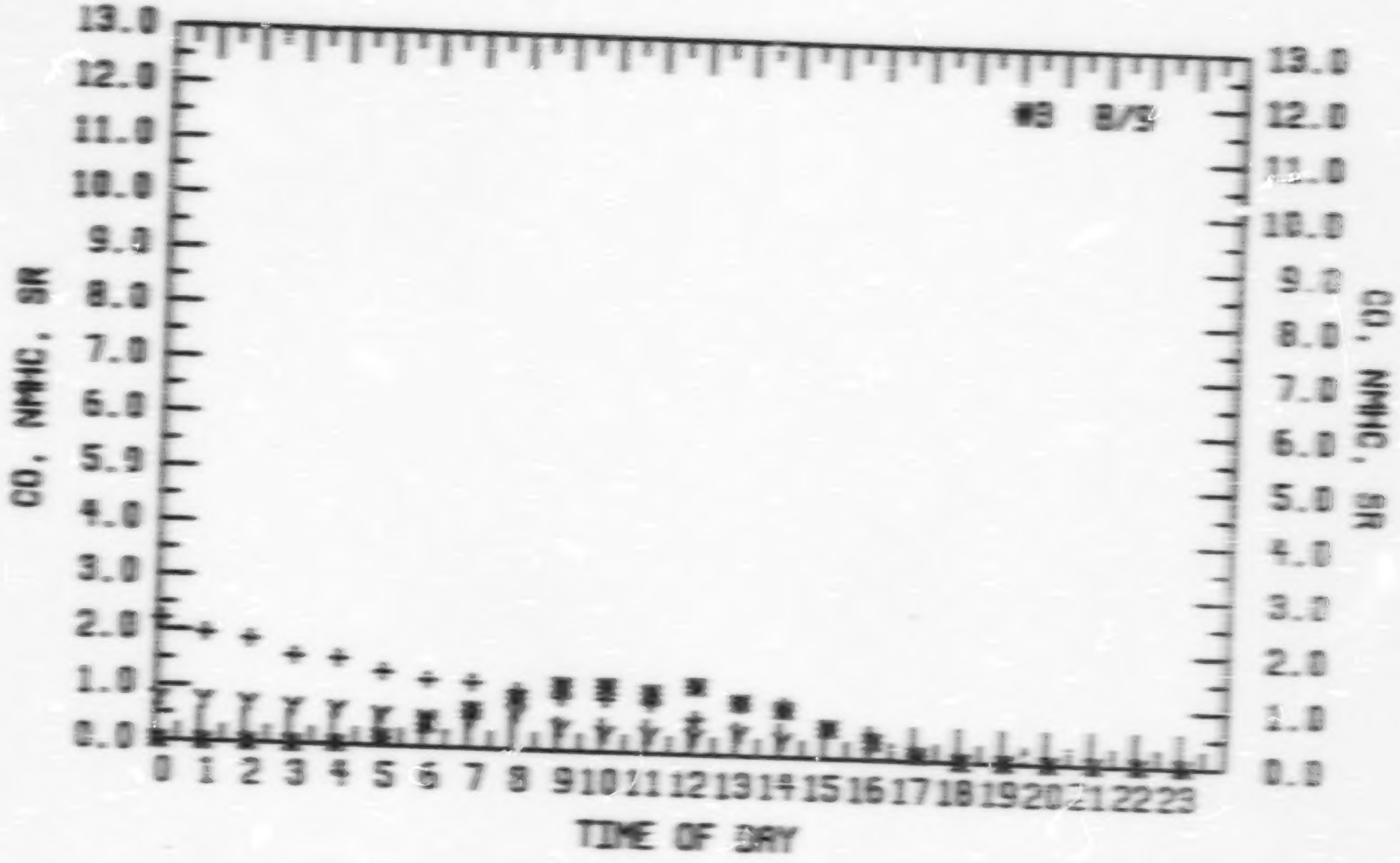

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.6
4.0
3.0
2.0
1.0
0.0
#2 9/18
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
CO, NMHC, SR

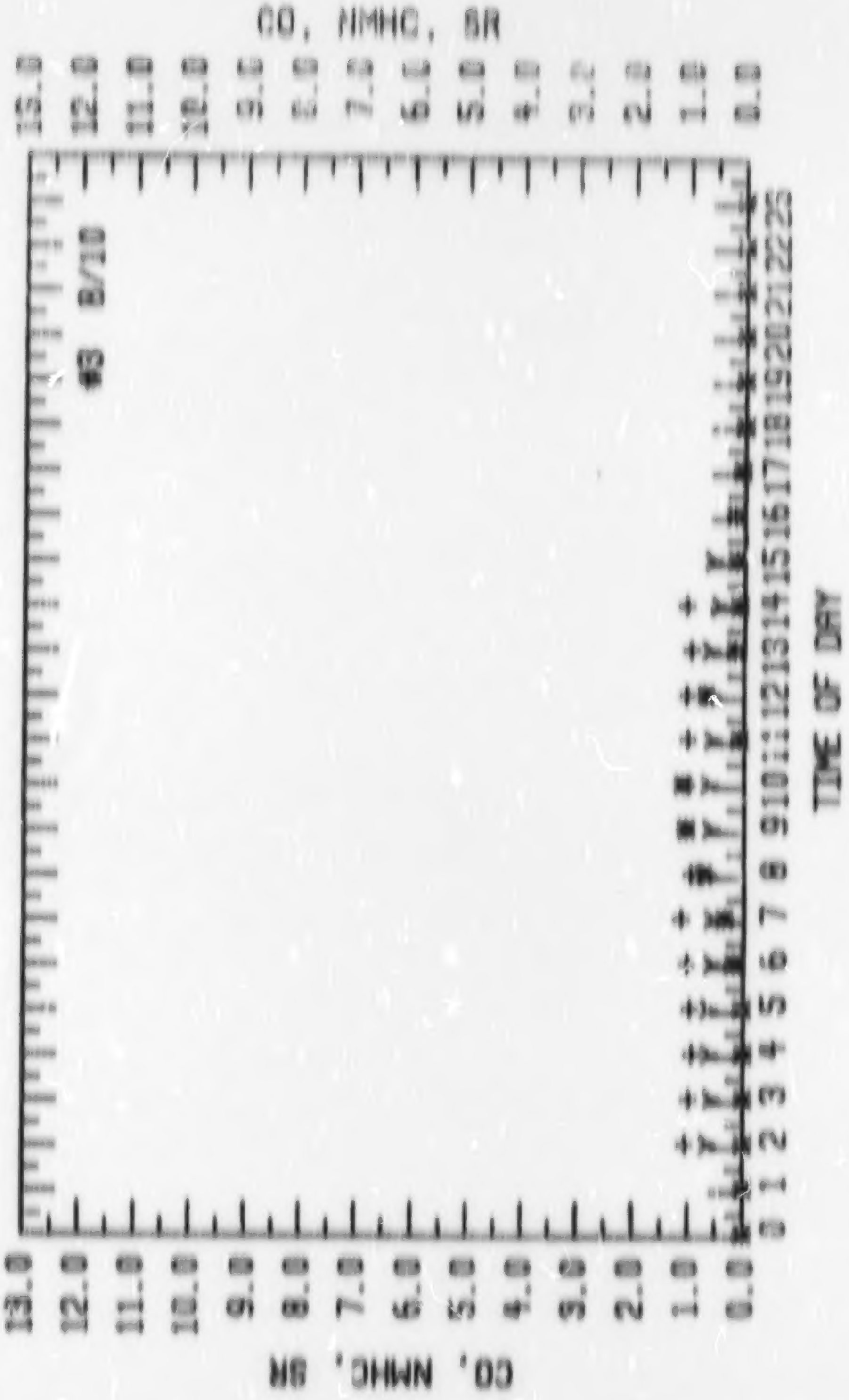
6/8 #G 772 @ NO₂ DIL. BEGAN 0940
O₃, NO, NO₂
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY

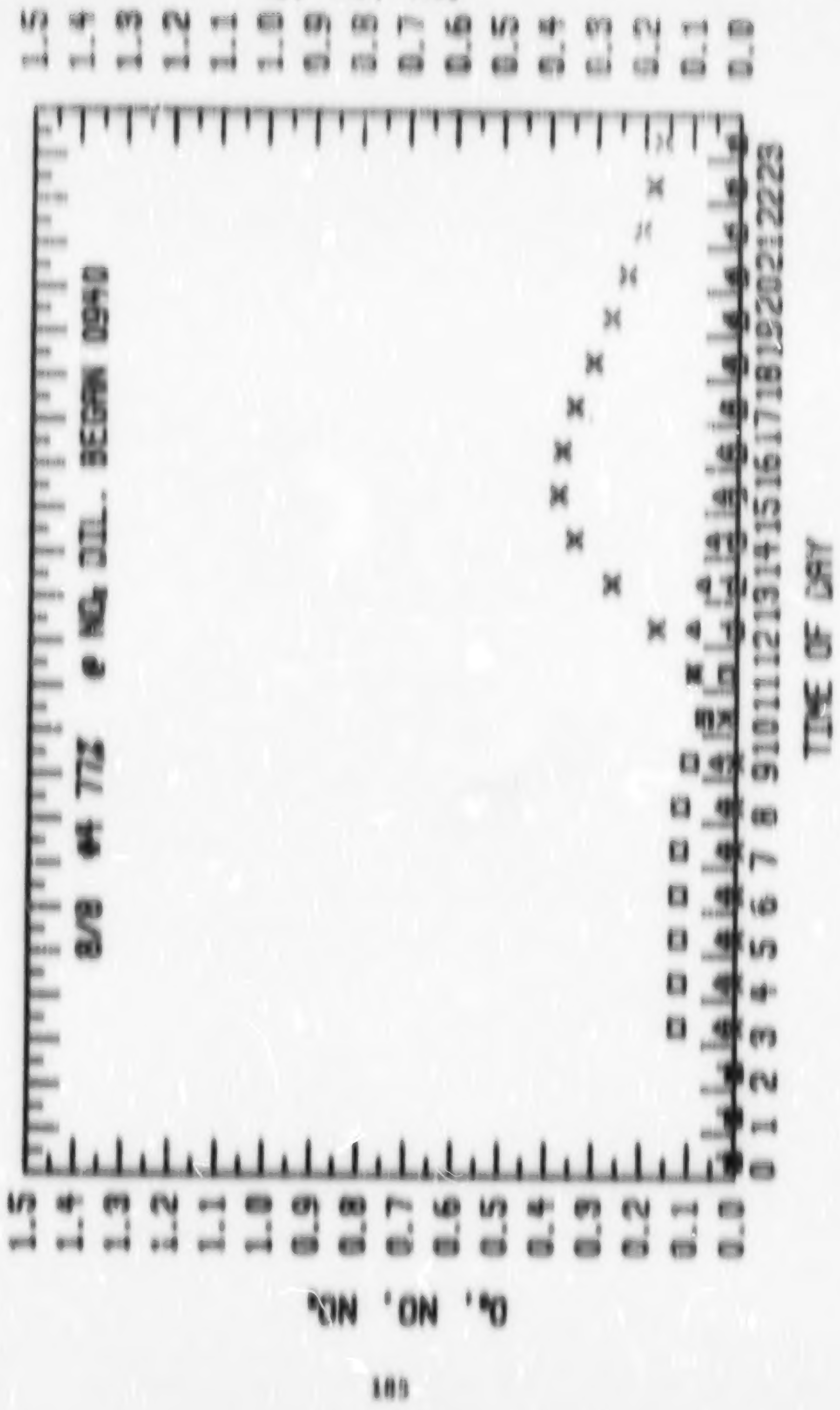

O3, NO, NO2
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
8/9 #3 TTZ @ NO2 DIL. ENDED 0940
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


8/10 #3 77%
⊕ NO_2
O_3, NO, NO_2
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#3 8/8
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR


CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.9
4.0
3.0
2.0
1.0
0.0
#3 8/9
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

CO, NMHC, SR
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
#3 8/10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR


8/8 #4 77Z @ NO$_2$ DIL. BEGAN 0940
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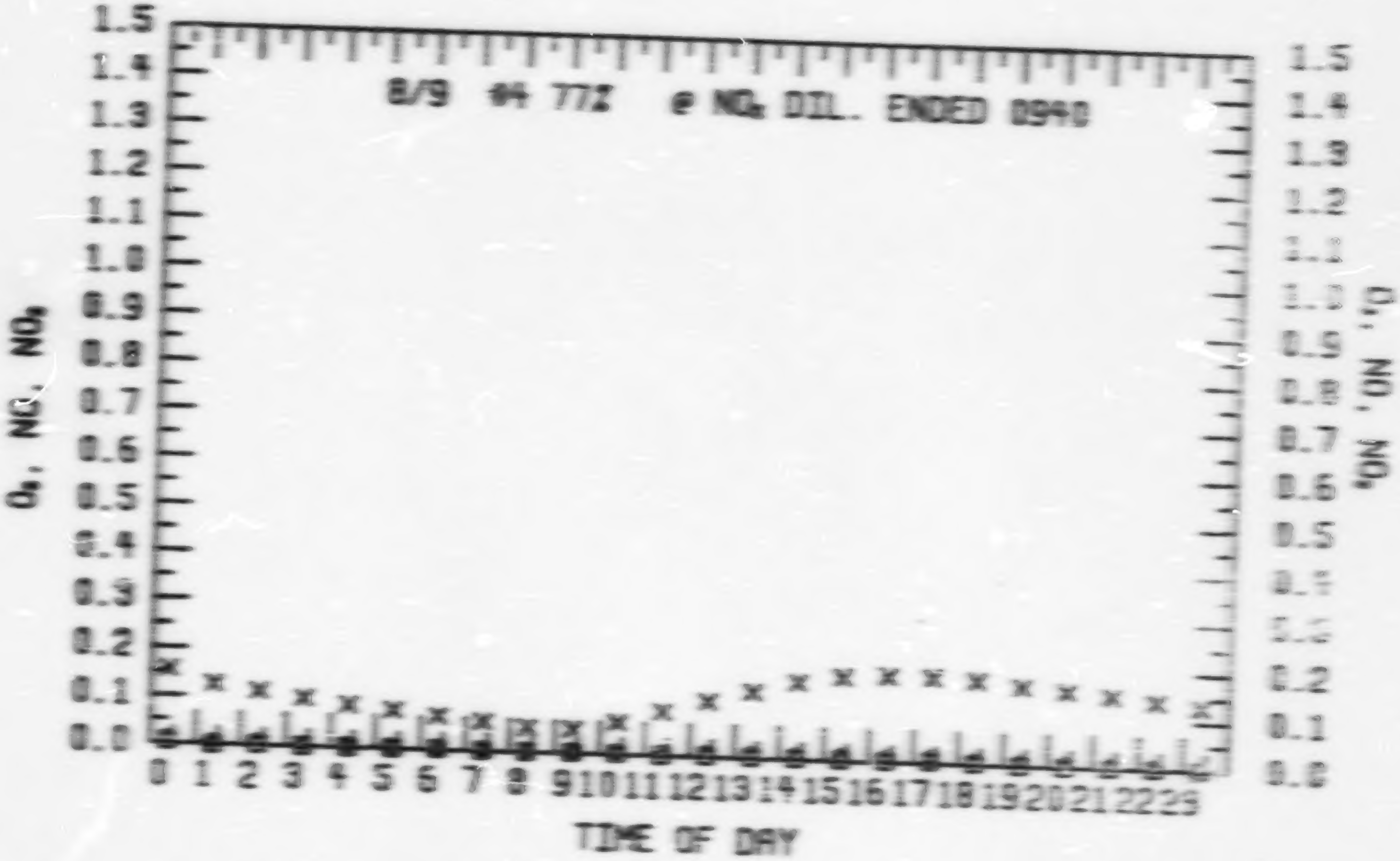
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


8/9 #4 77% @ NO₂ DIL. ENDED 0940
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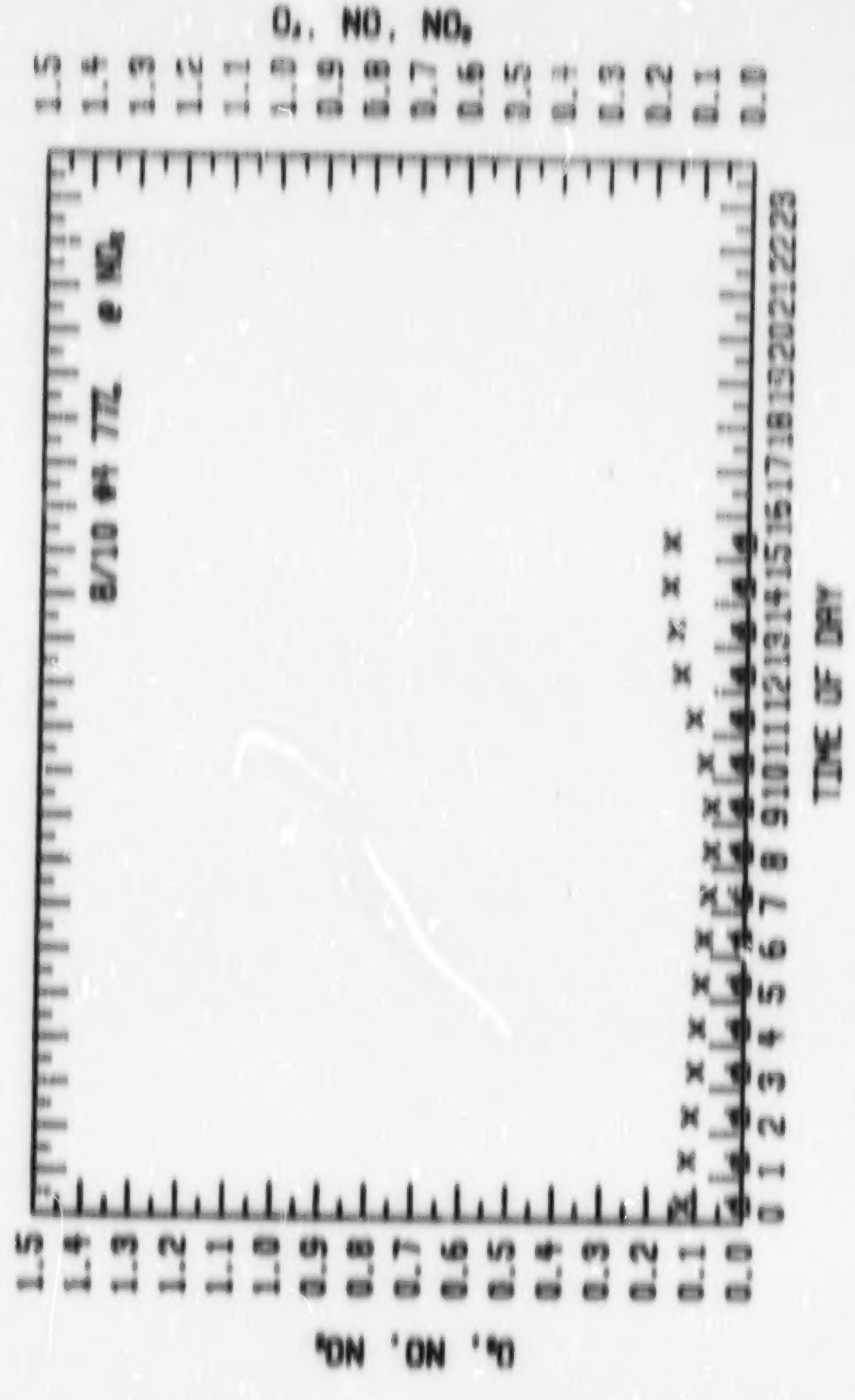
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY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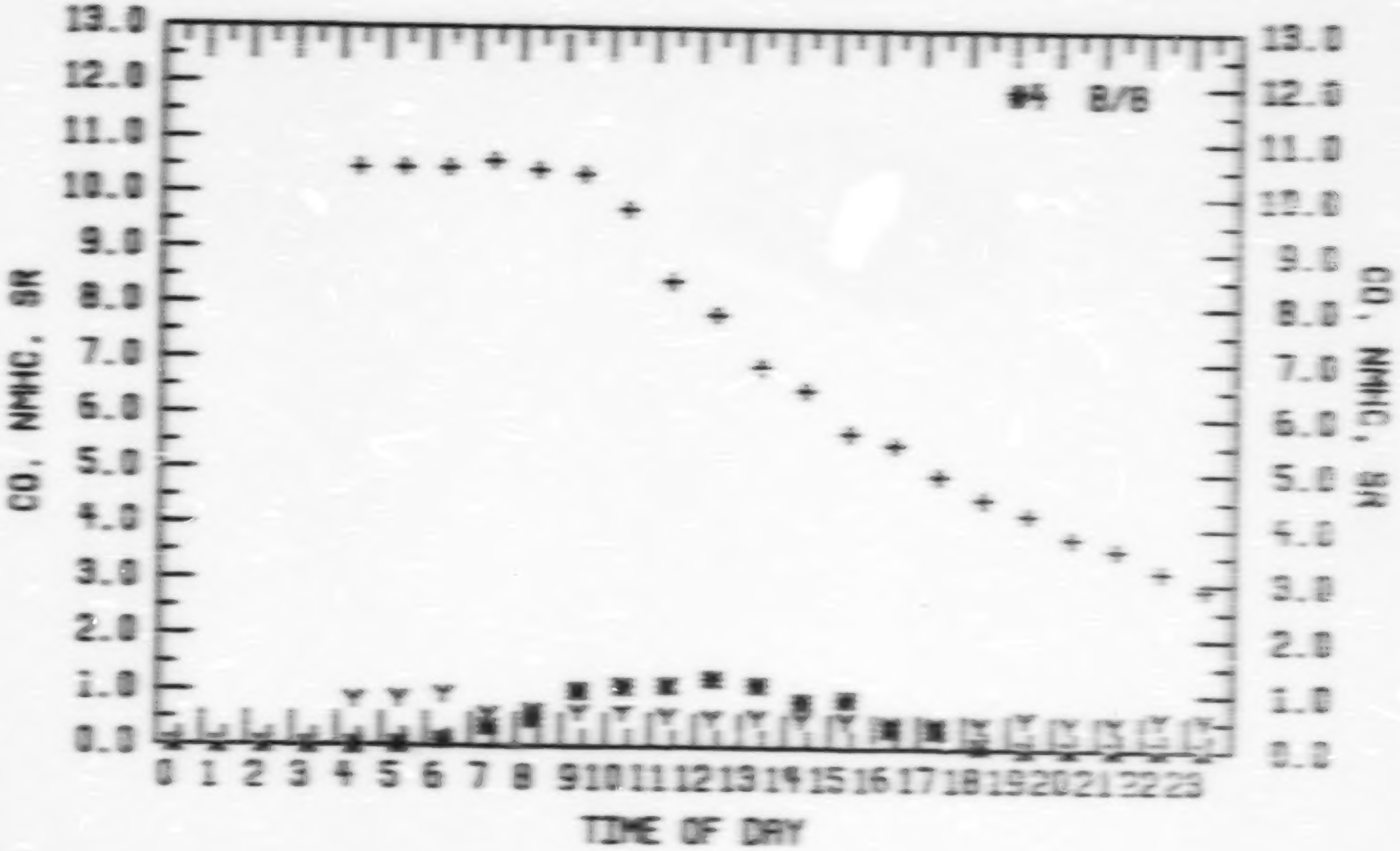
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8/10 #4 77Z
@ NO2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY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10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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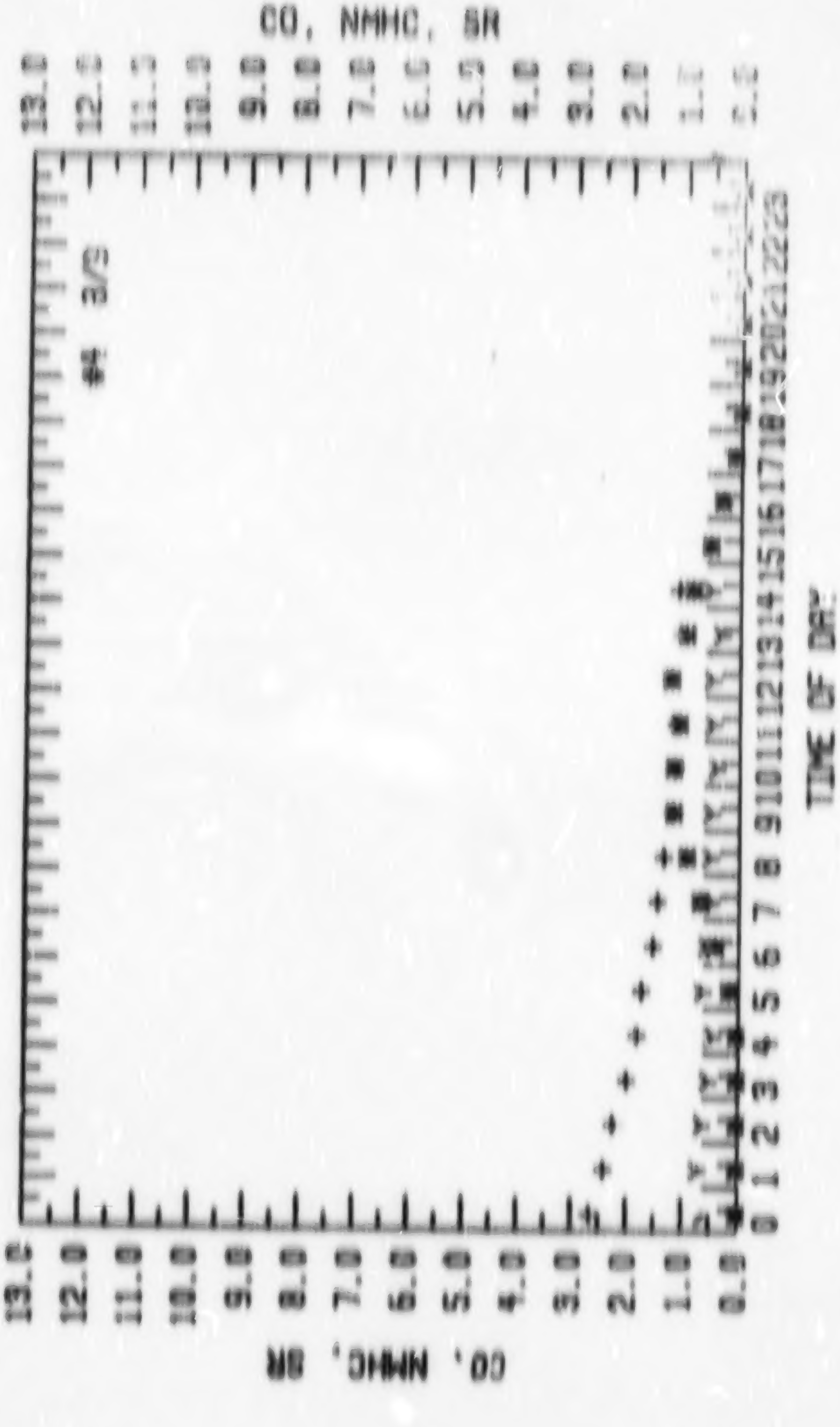
CO, NMHC, SR
#4 8/8
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY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11.0
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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#4 3/3
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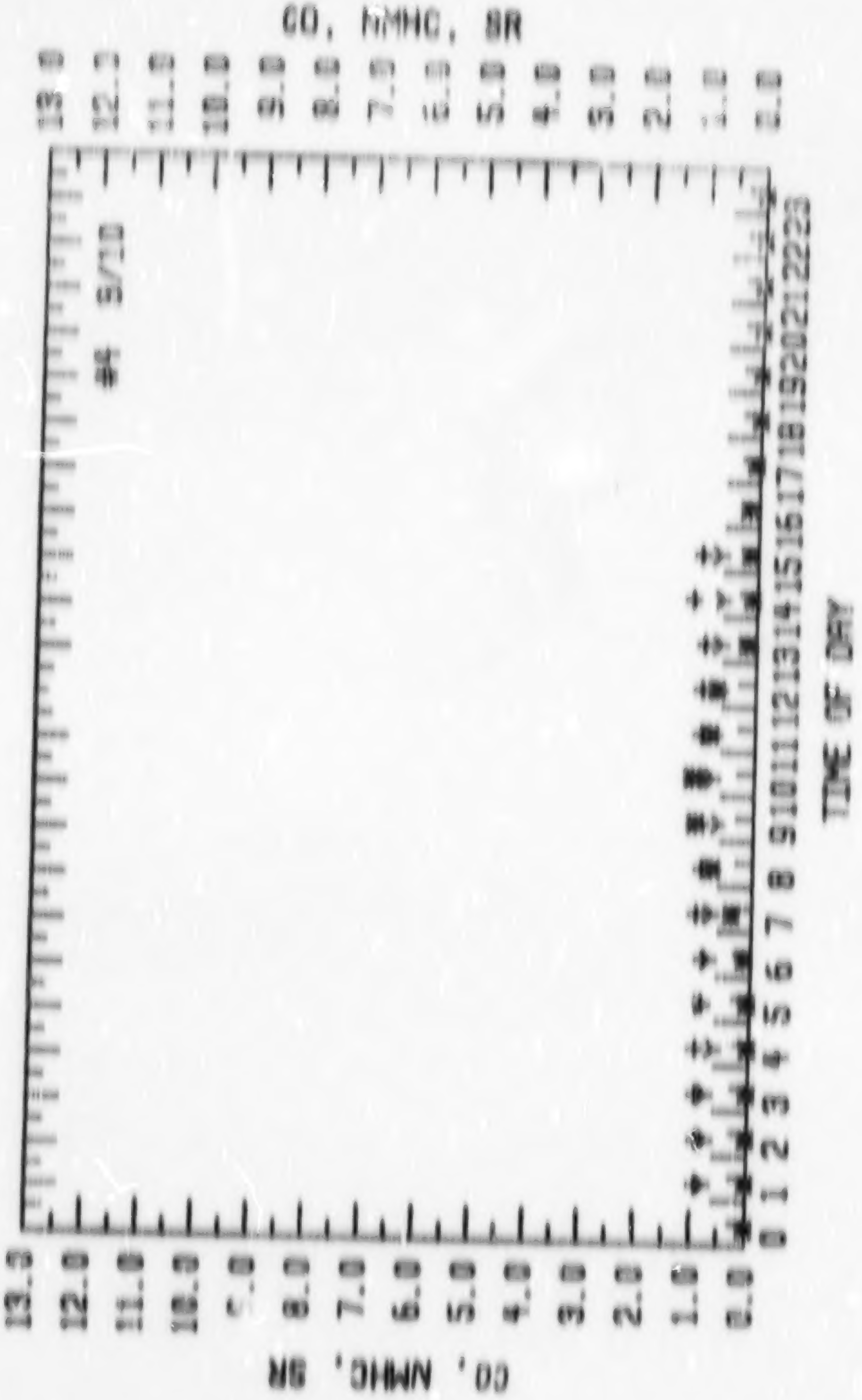
TIME OF DAY
CO, NMHC, SR


CO, NMHC, SR
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11.0
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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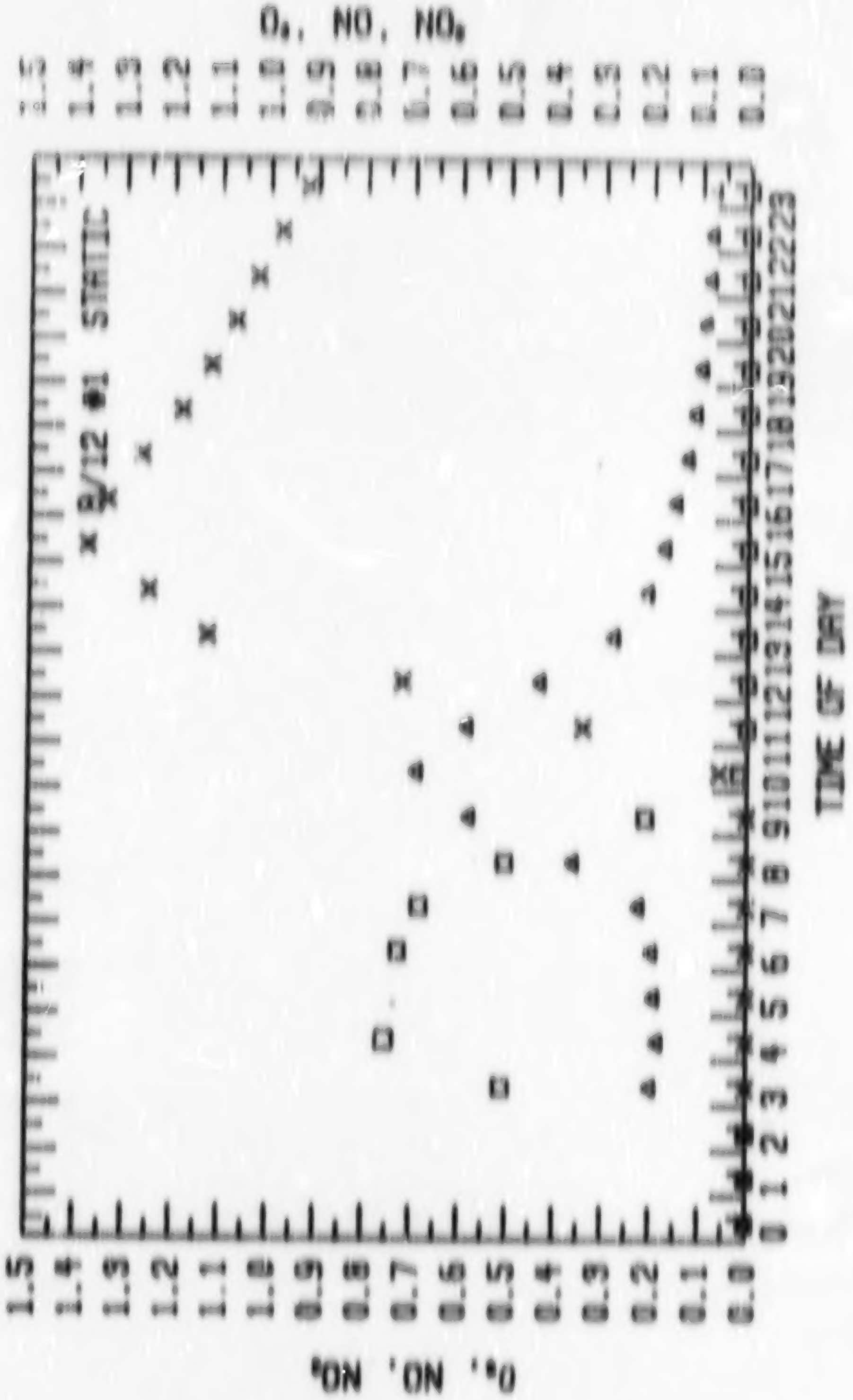
#4 9/10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR



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0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8/12 #1 STATIC
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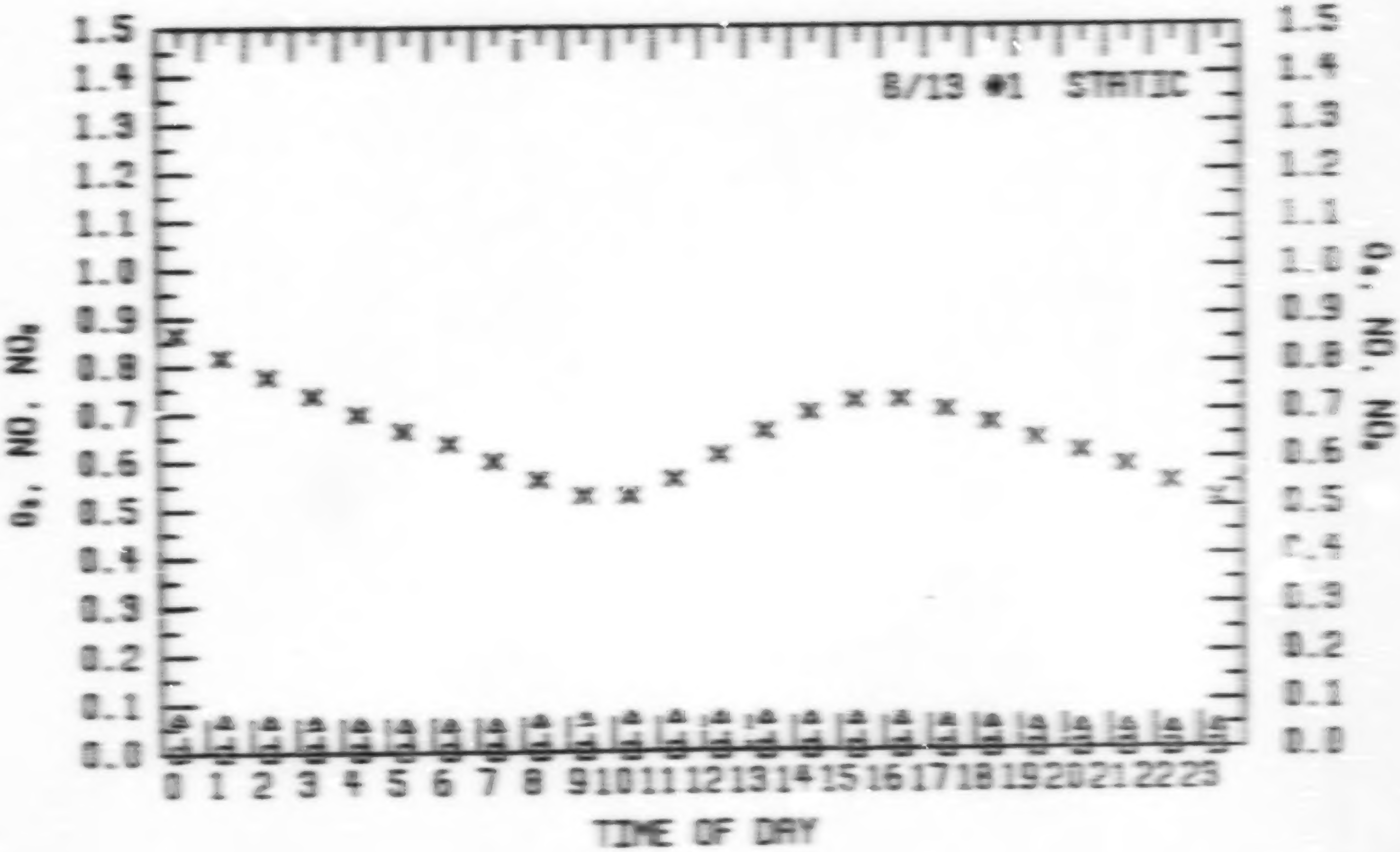
TIME OF DAY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1.3
1.2
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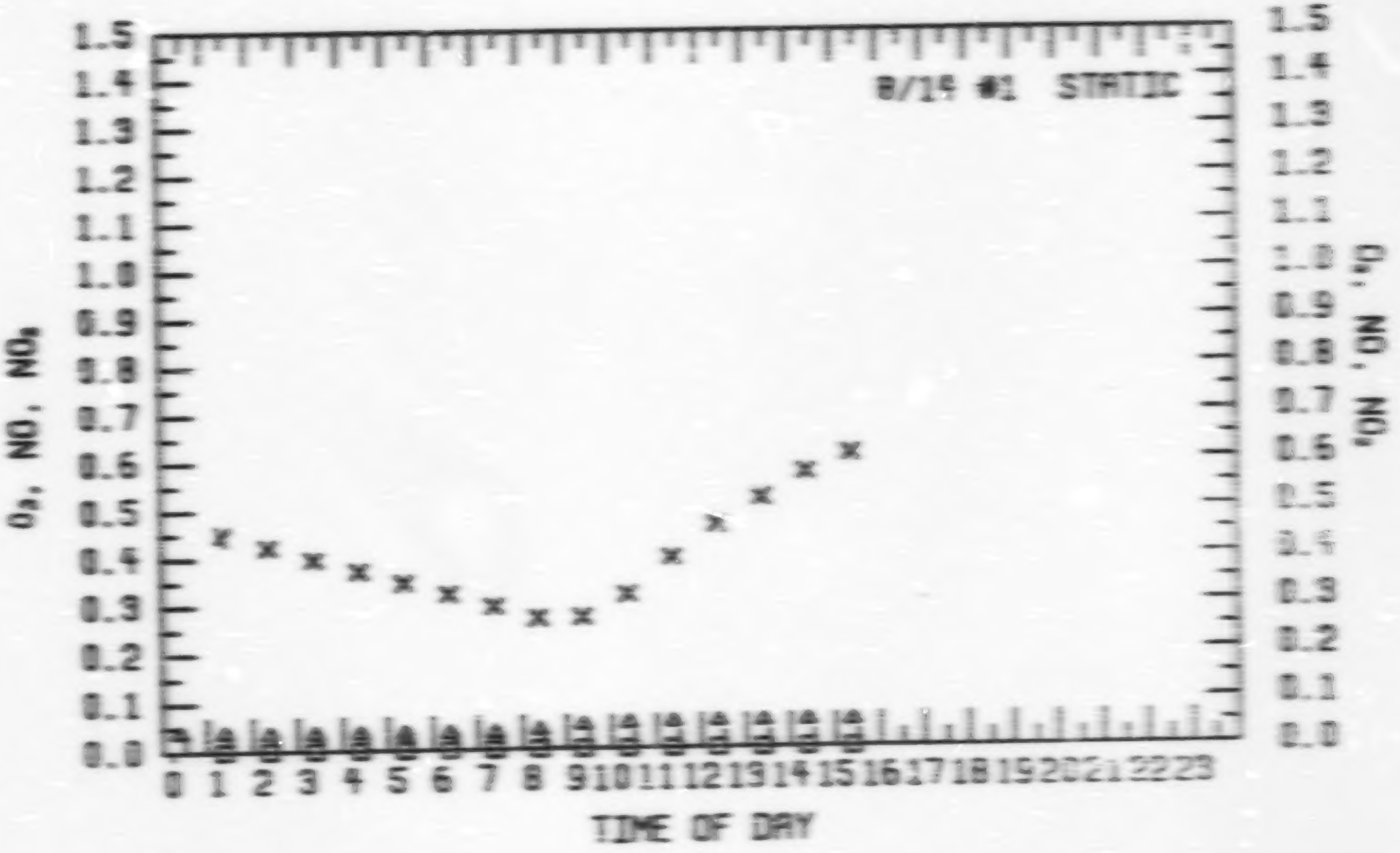
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


8/14 #1 STATIC
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1.3
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1.0
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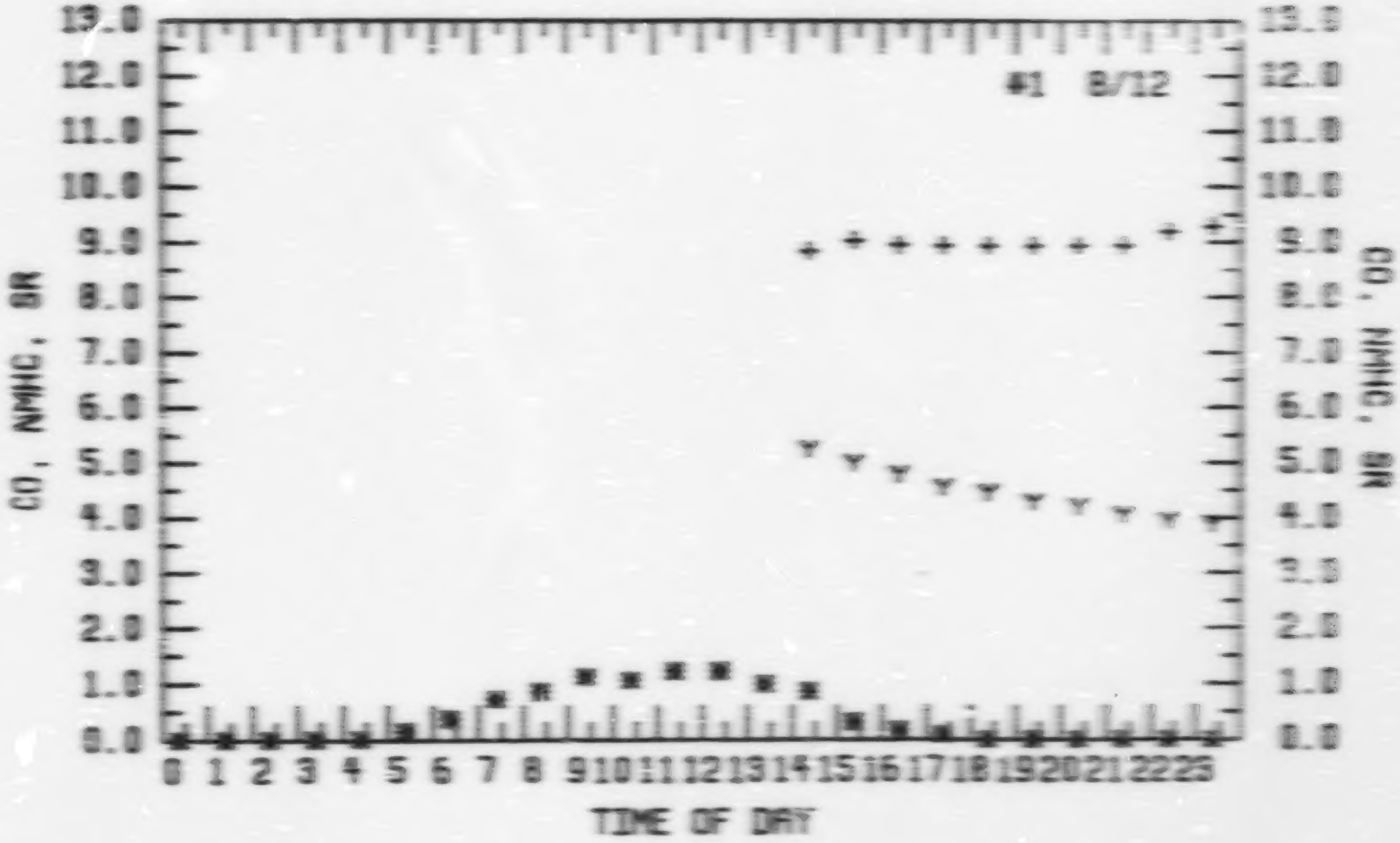
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY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4.0
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6.0
7.0
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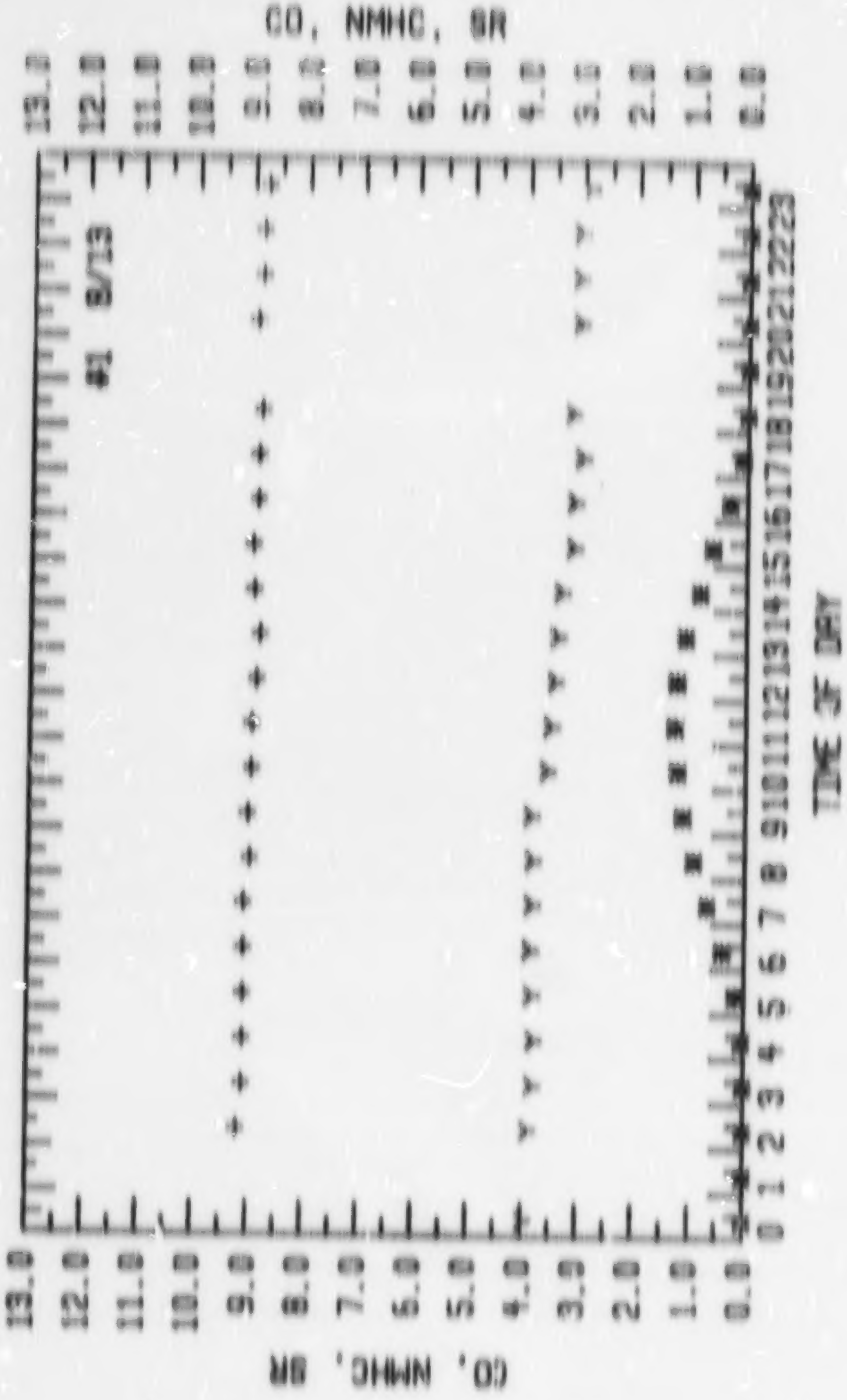
10.0
11.0
12.0
13.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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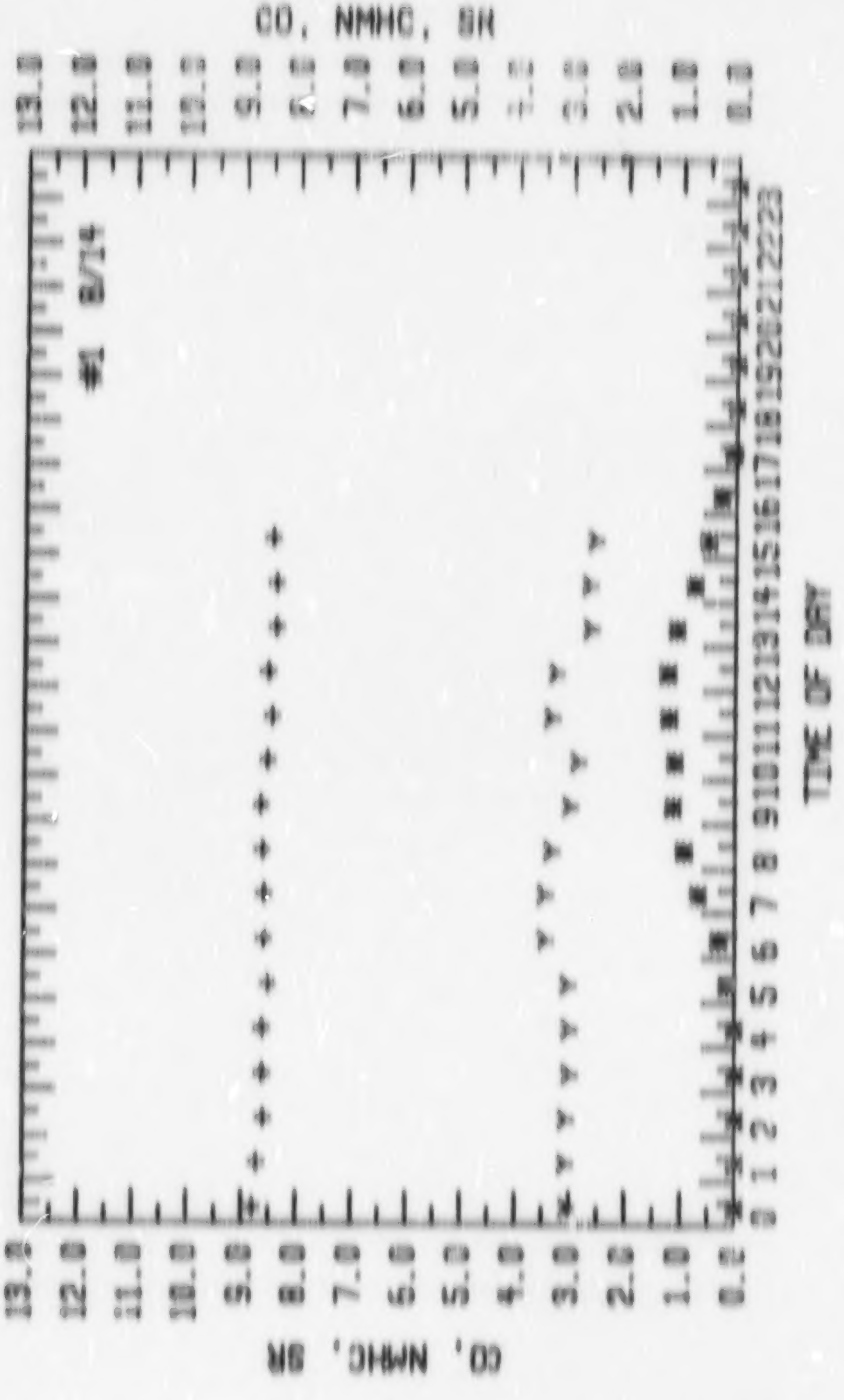
#1 9/13
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR


CO, NMHC, SR
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8.0
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5.0
4.0
3.0
2.0
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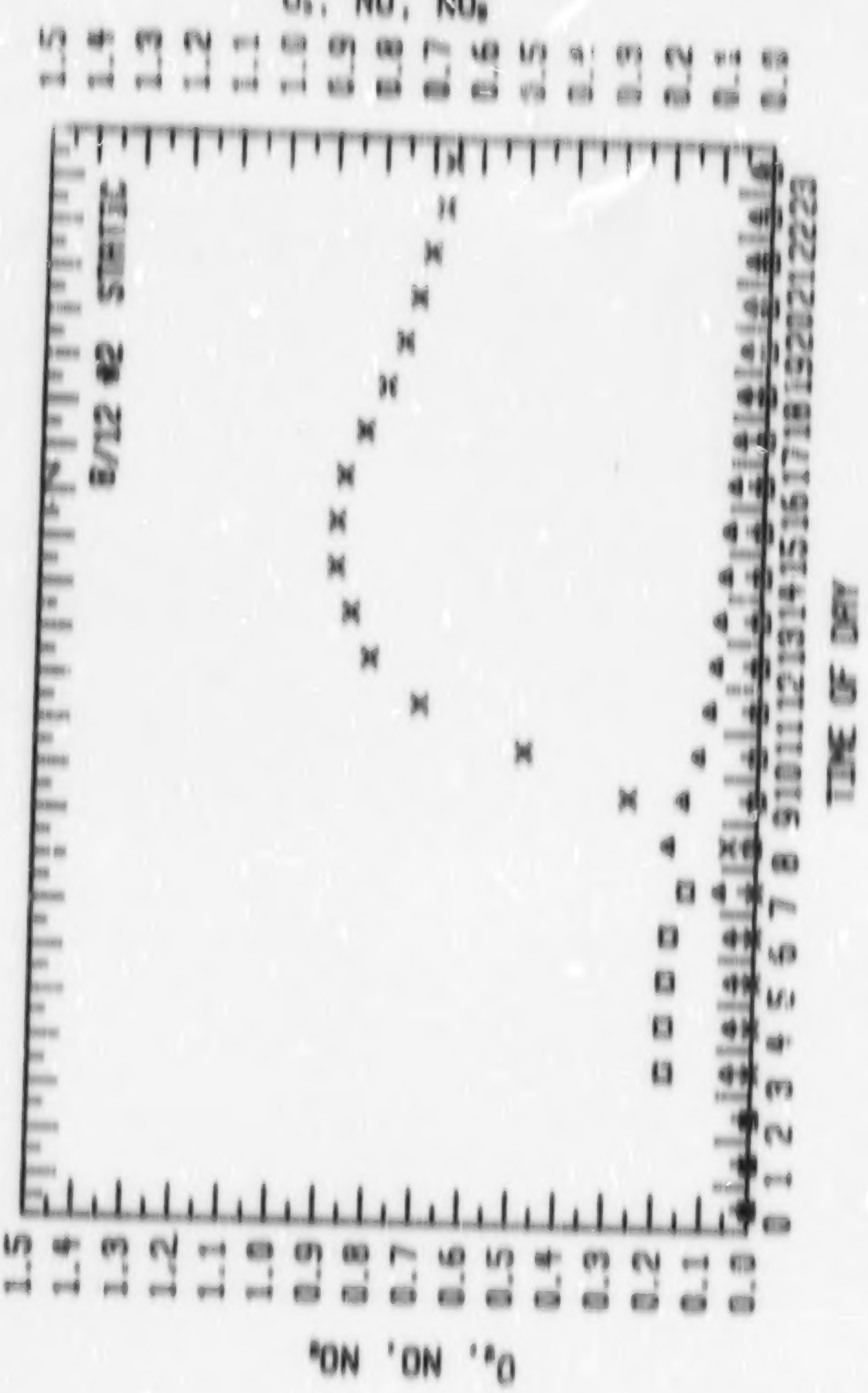
#1 8/14
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY
CO, NMHC, SR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0.7
0.8
0.9
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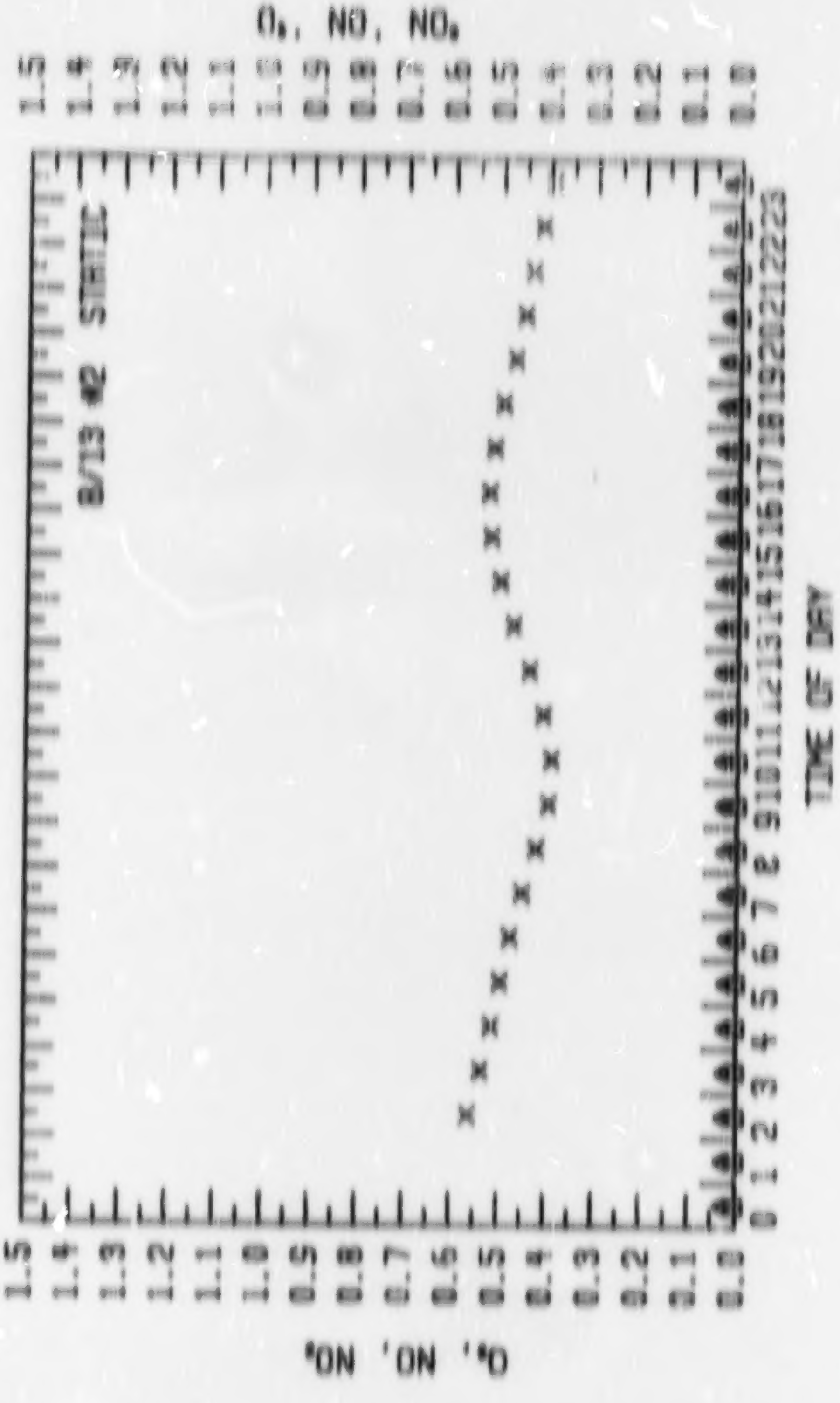
1.1
1.2
1.3
1.4
1.5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


O3, NO, NO2
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1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8/13 #2 STATIC
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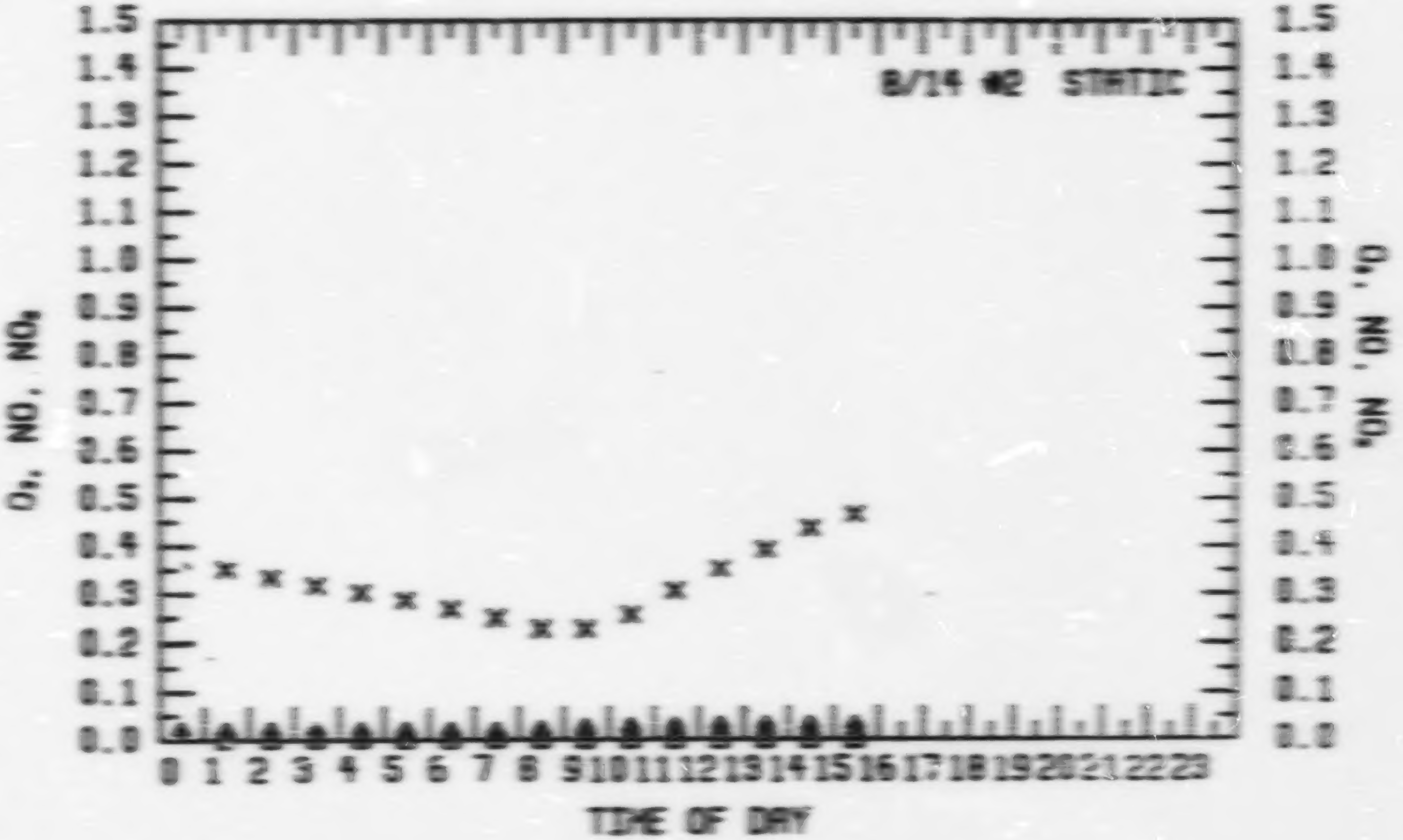
TIME OF DAY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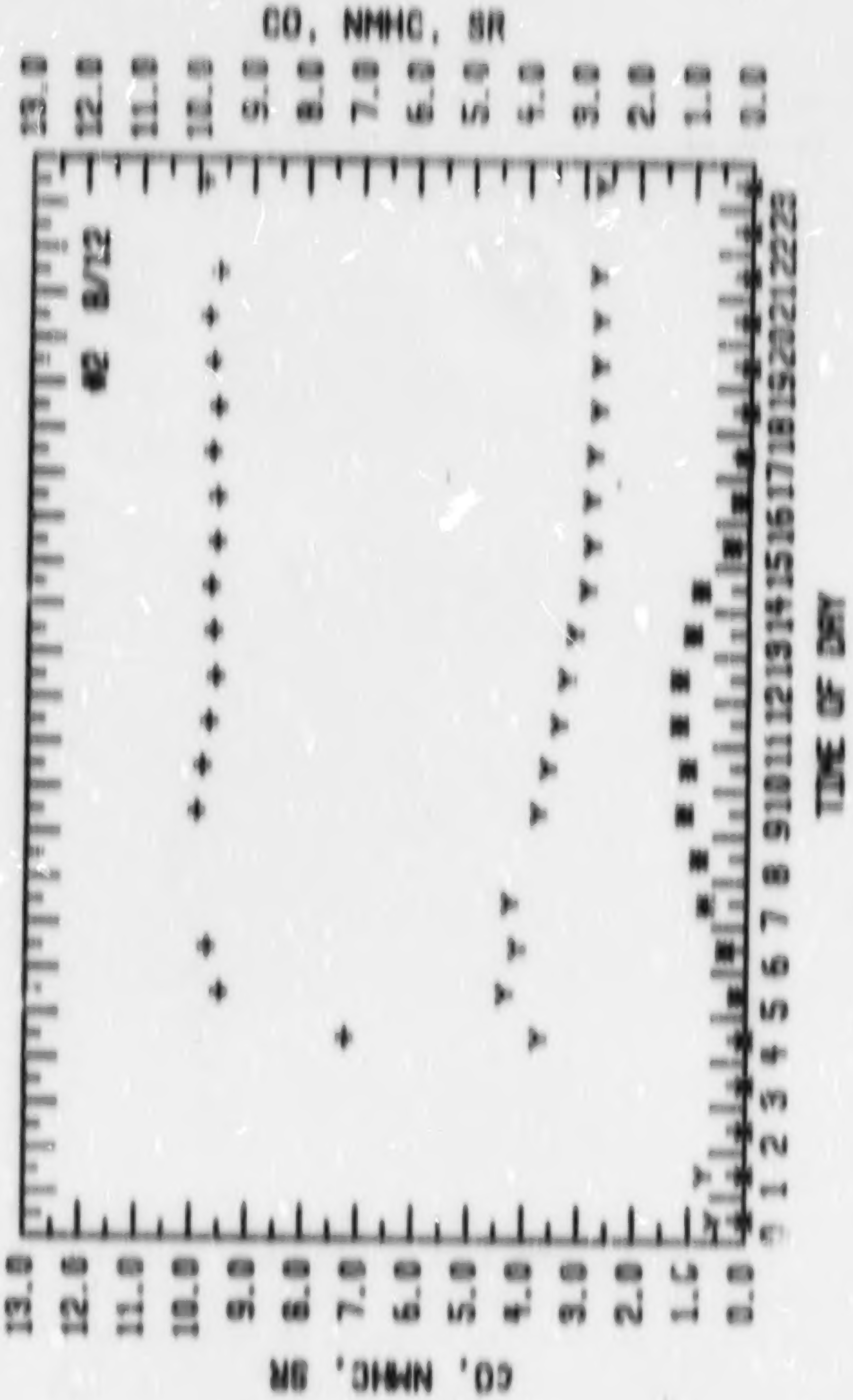
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
#2 8/12
TIME OF DAY
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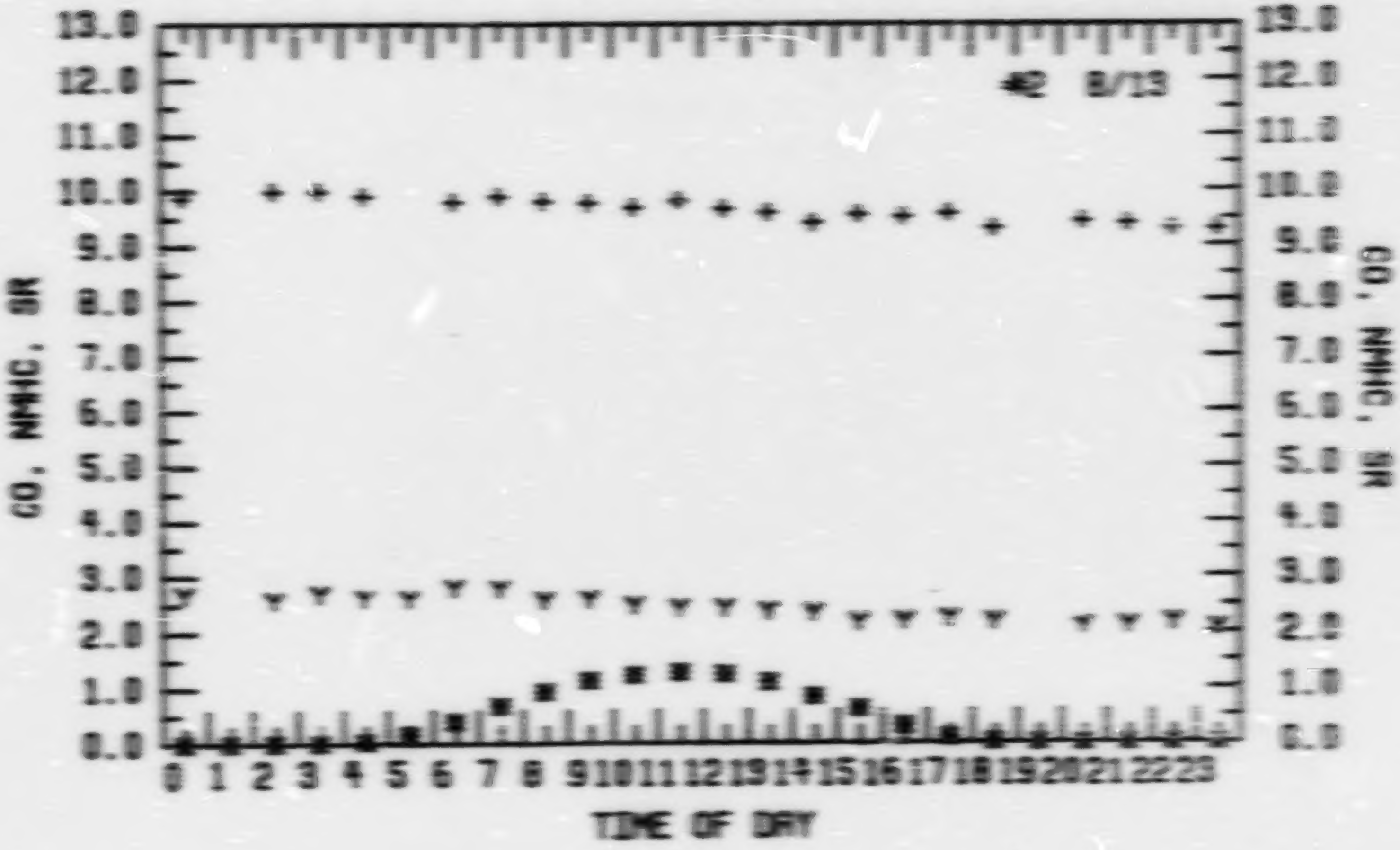
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0


#2 8/13
CO, NMHC, SR
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9.0
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7.0
6.0
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2.0
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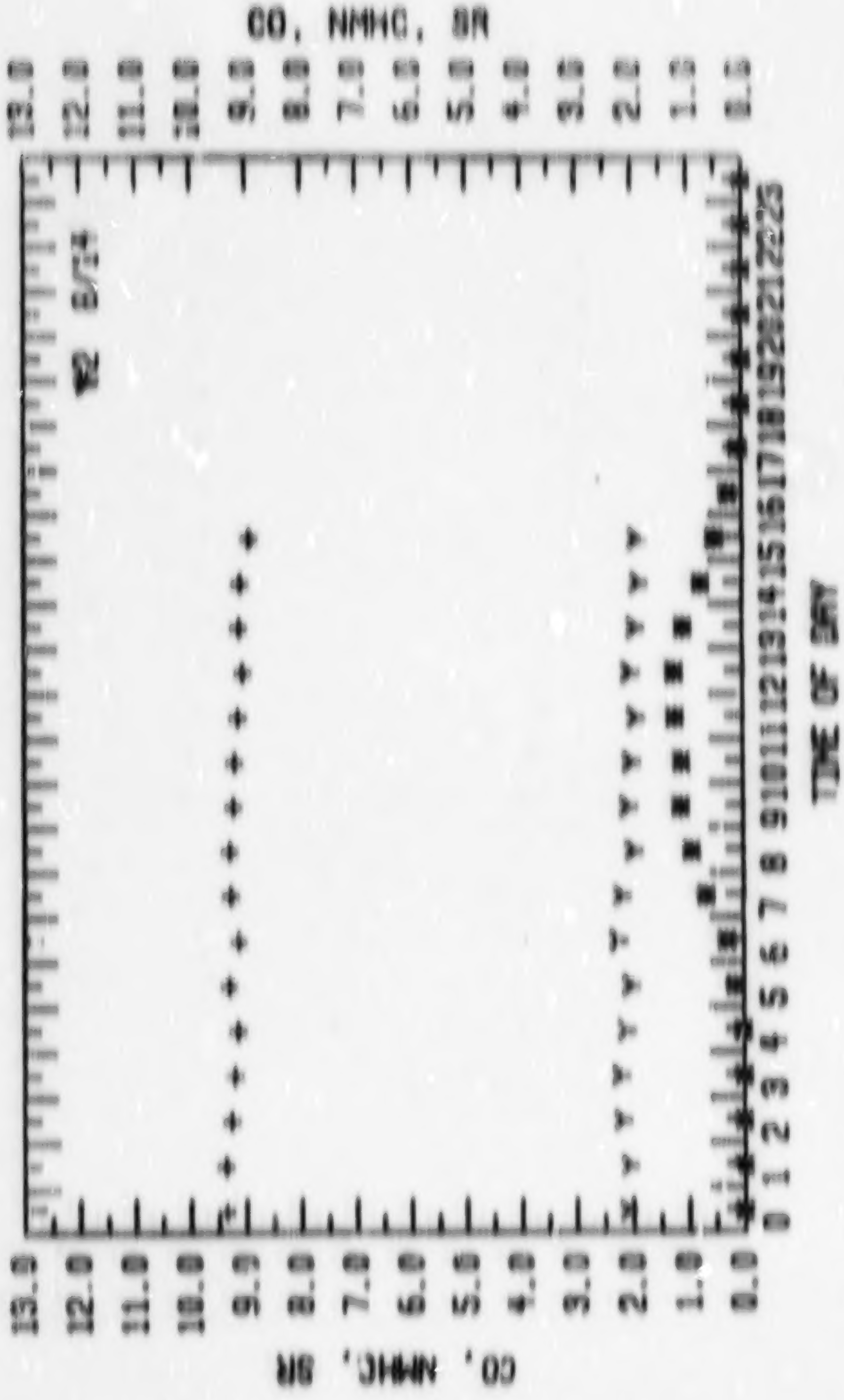
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
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6.0
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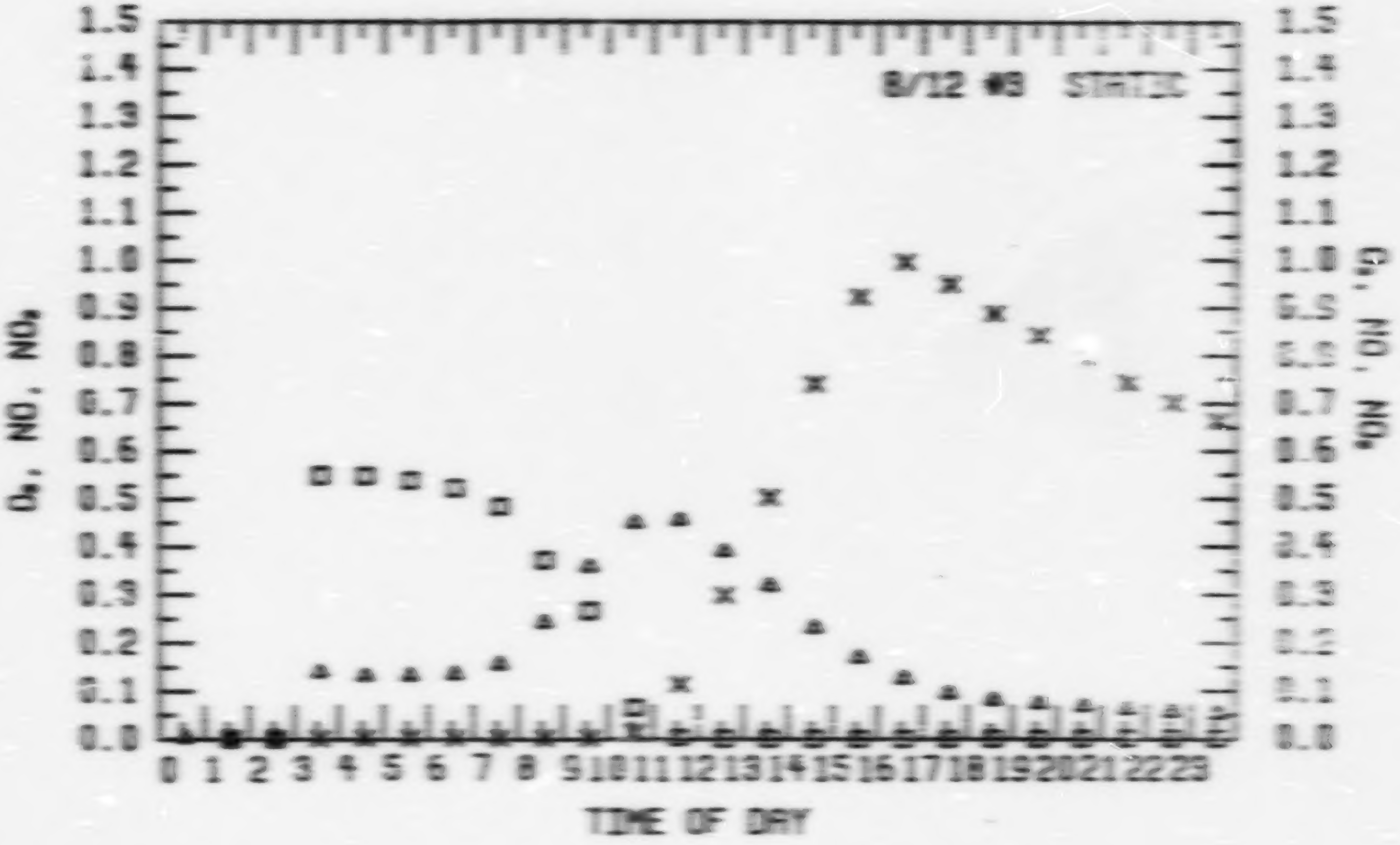
1.0
0.0
T2 8/24
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY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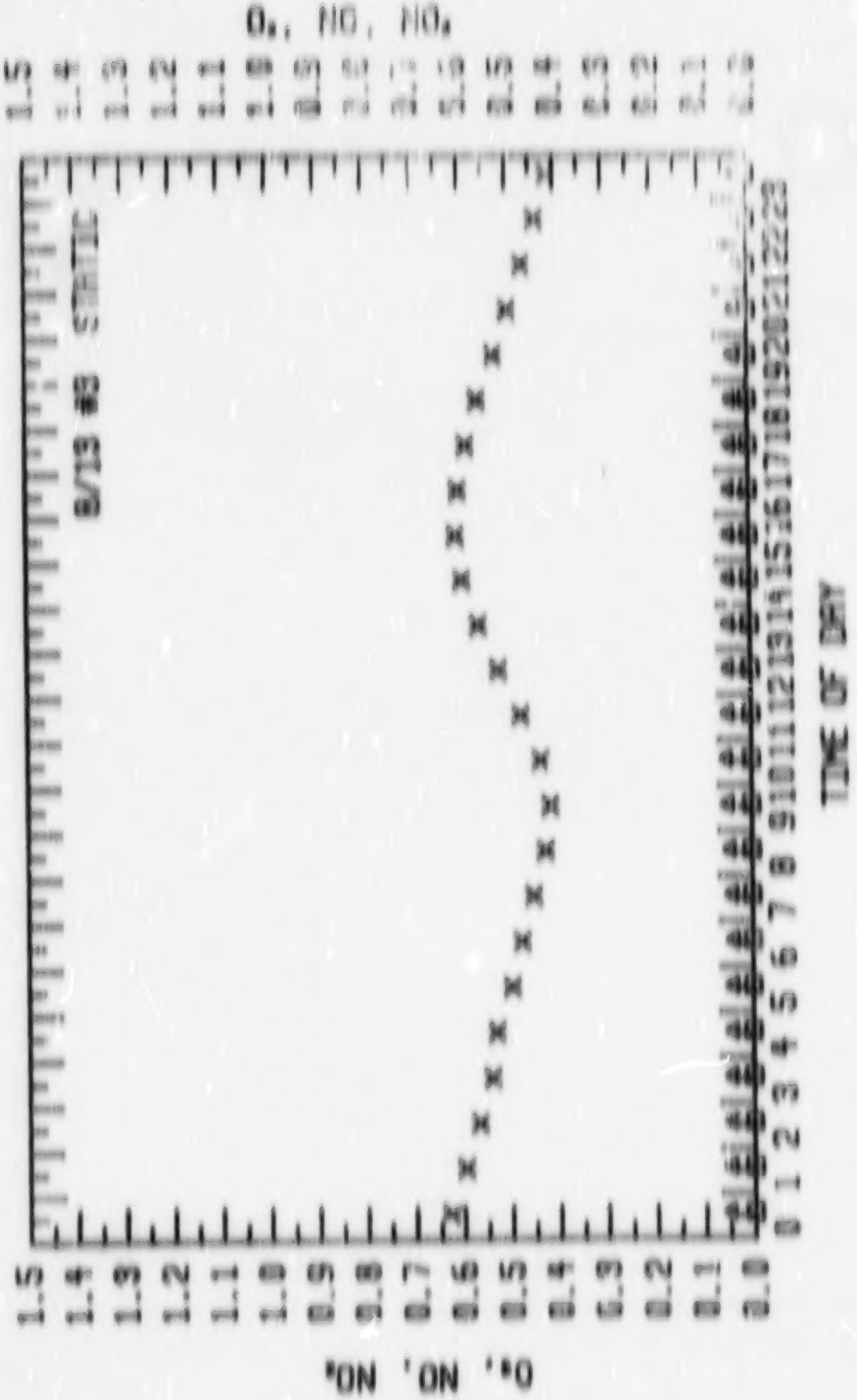
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


9/13 #3 STATIC
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0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
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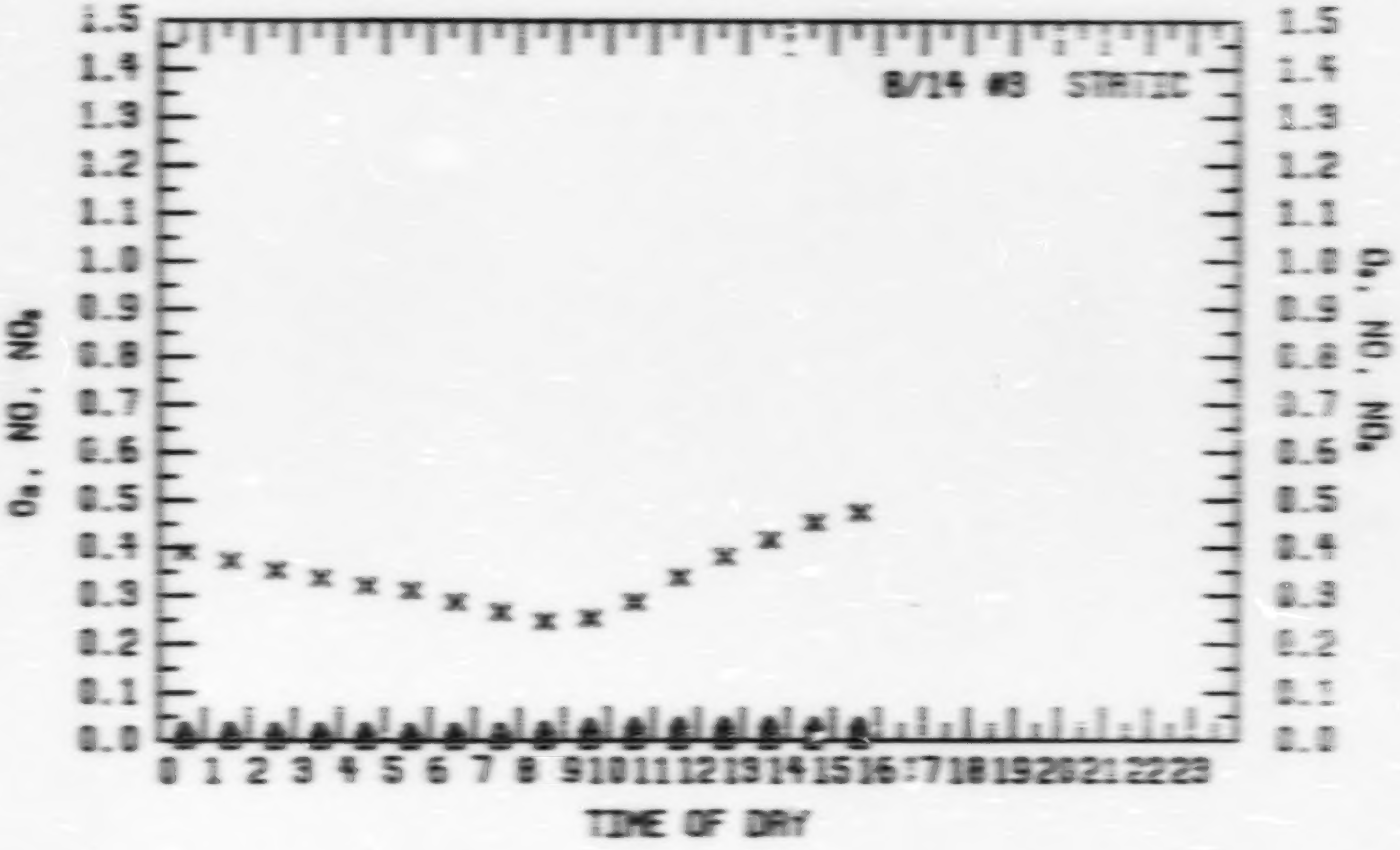
1.2
1.3
1.4
1.5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


8/14 #3 STATIC
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1.4
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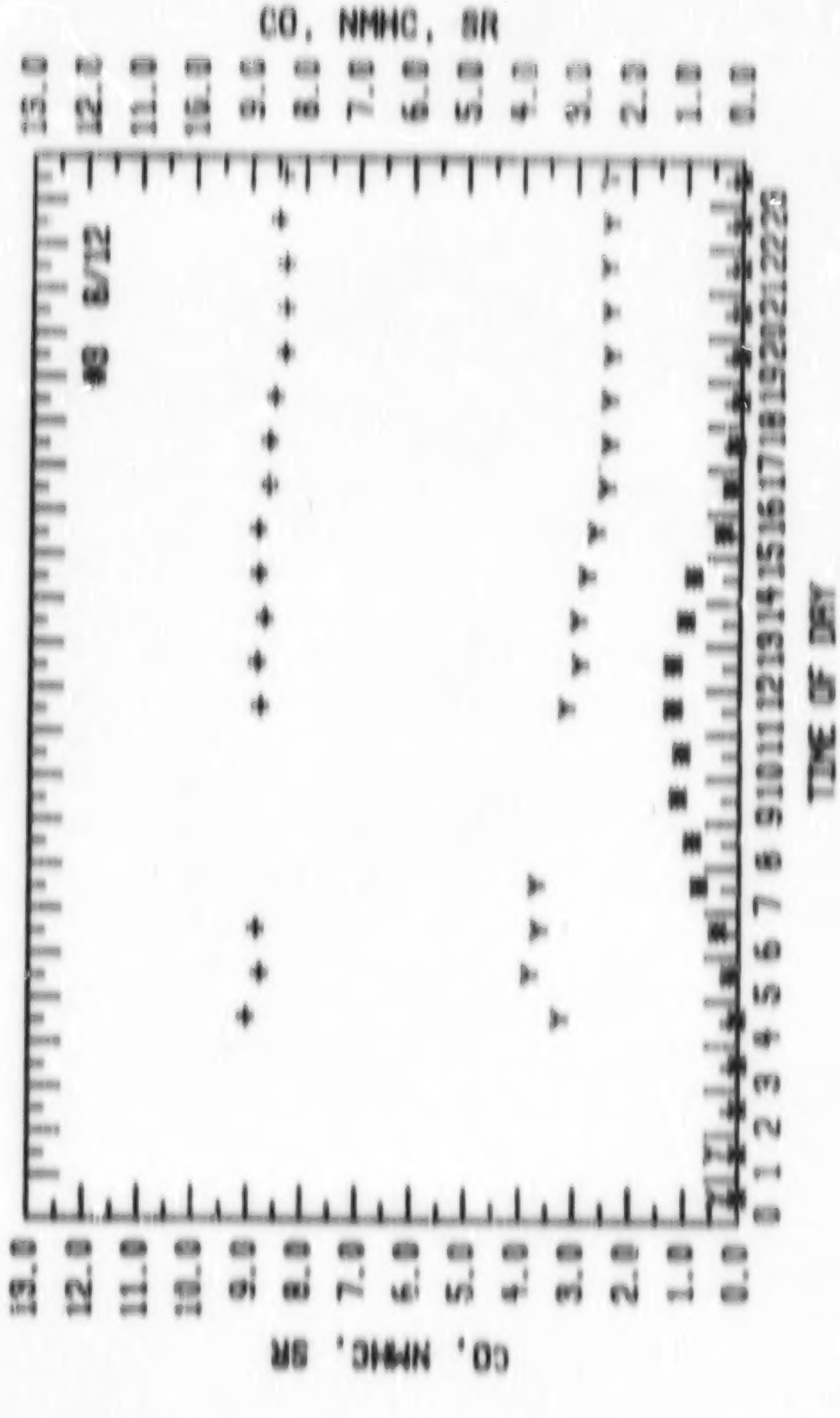
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


CO, NMHC, SR
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8.0
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6.0
5.0
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1.0
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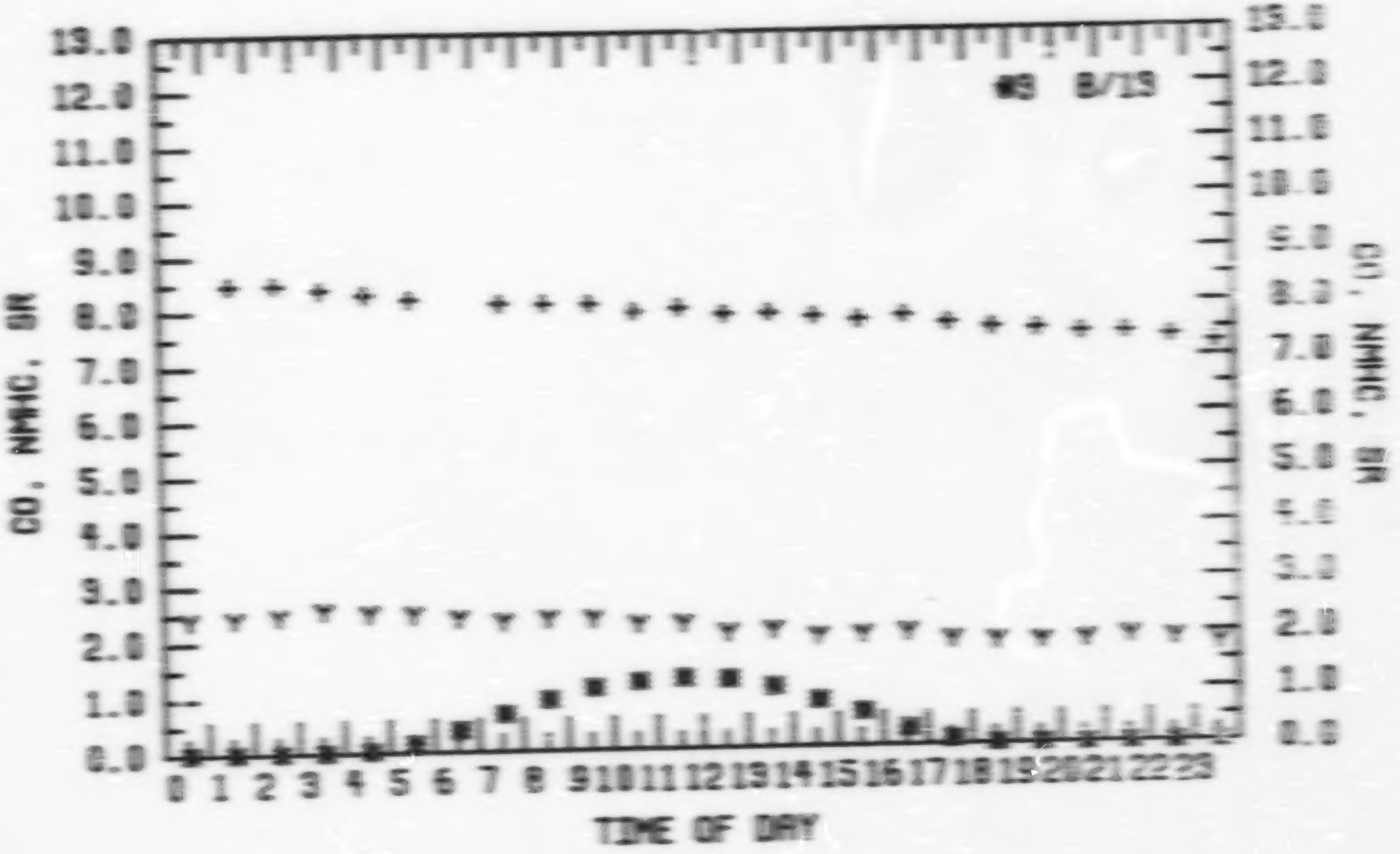
WS 6/12
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#3 8/19
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2.0
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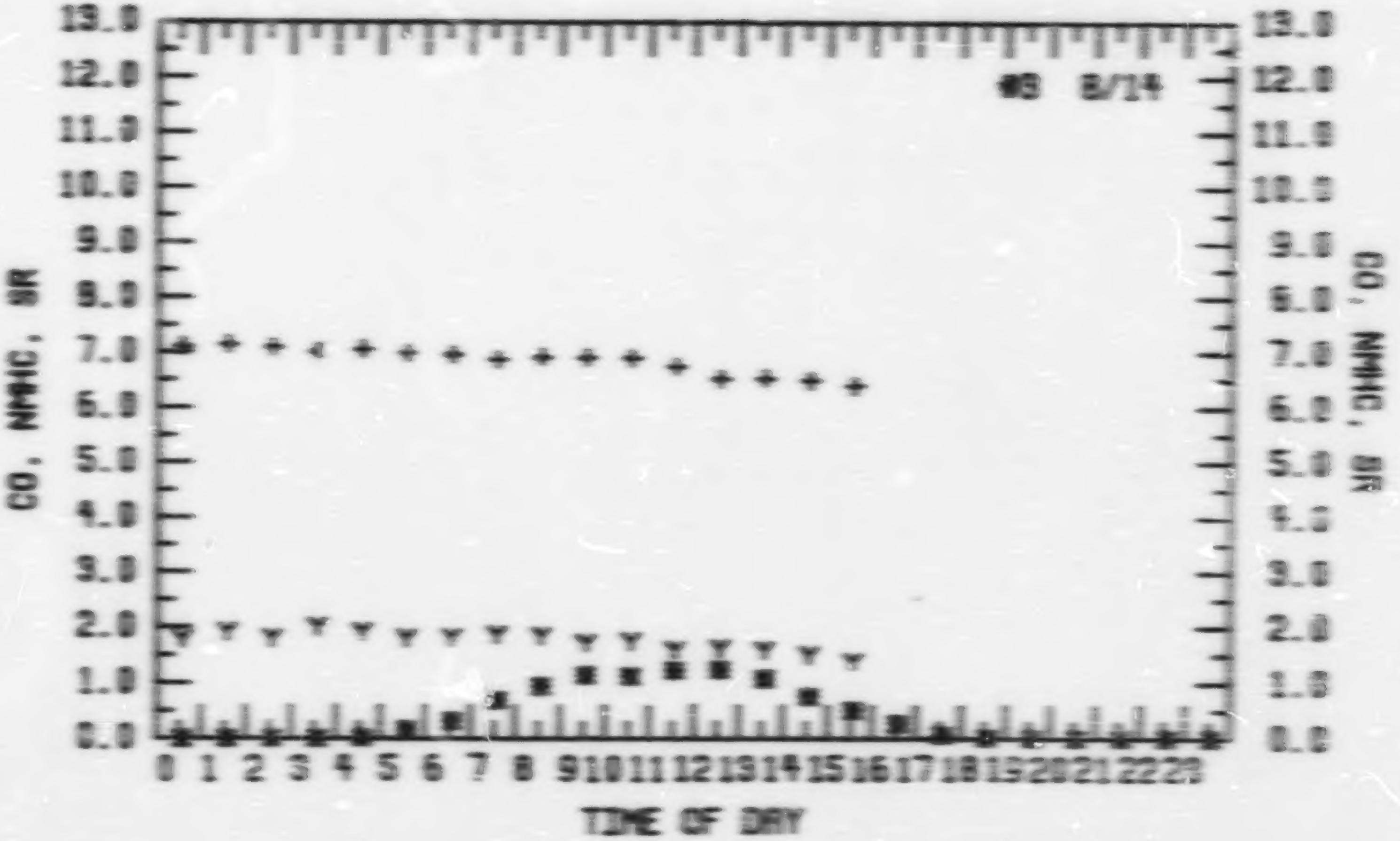
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY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7.0
6.0
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2.0
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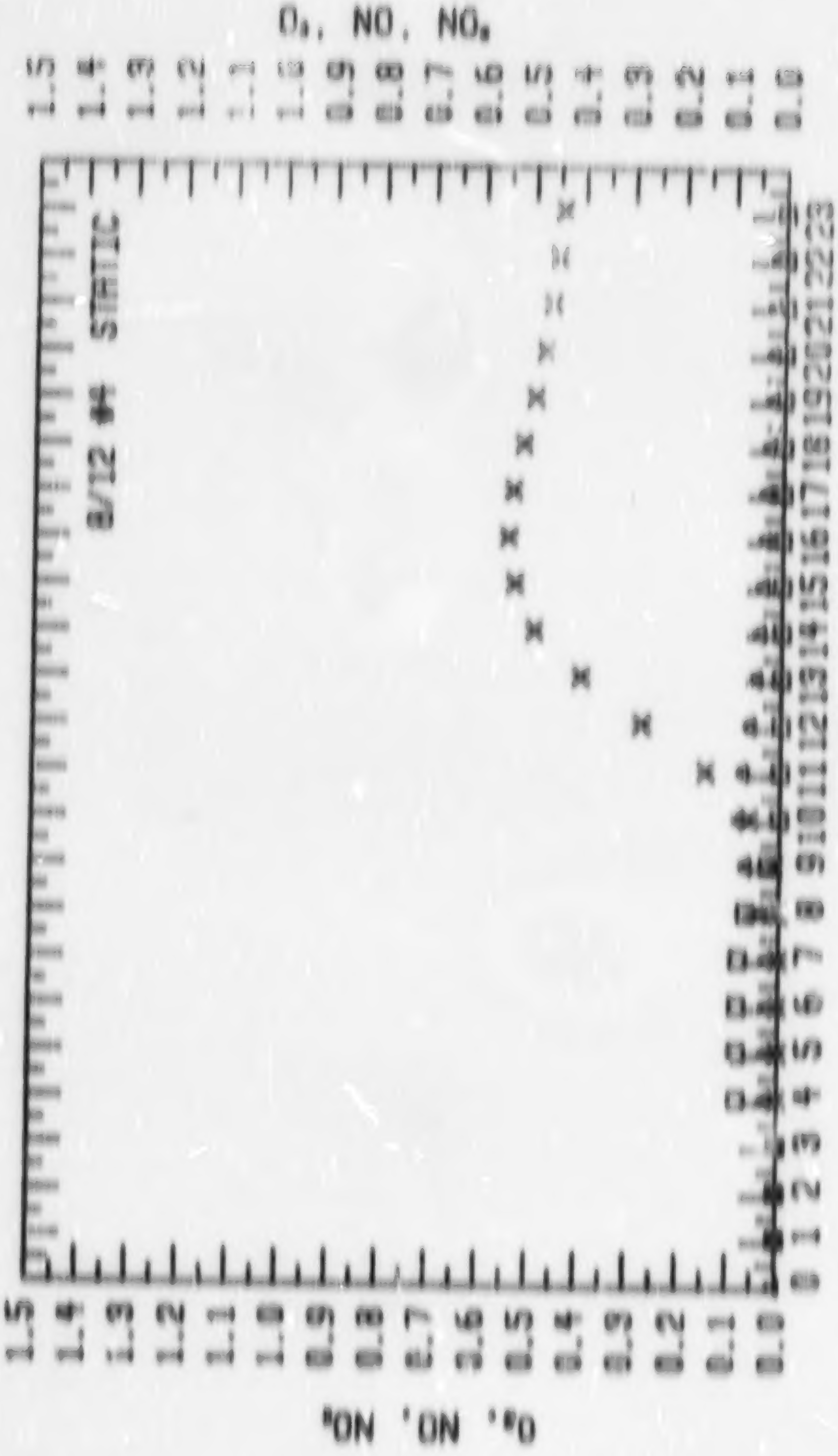
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


8/12 #4 STATIC
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0.7
0.6
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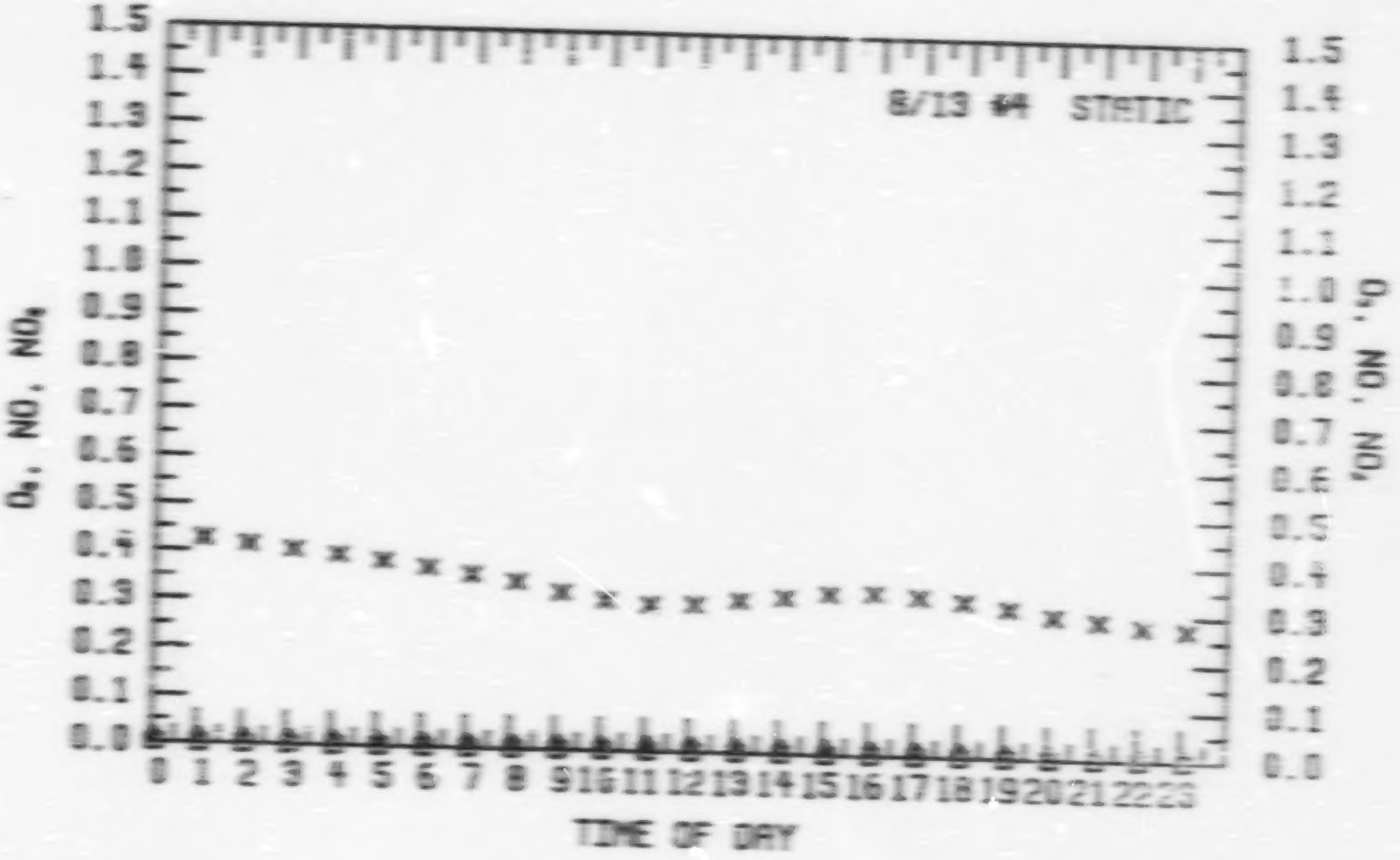
0.2
0.1
0.0
TIME OF DAY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23


8/13 #4 STATIC
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1.2
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1.0
0.9
0.8
0.7
0.6
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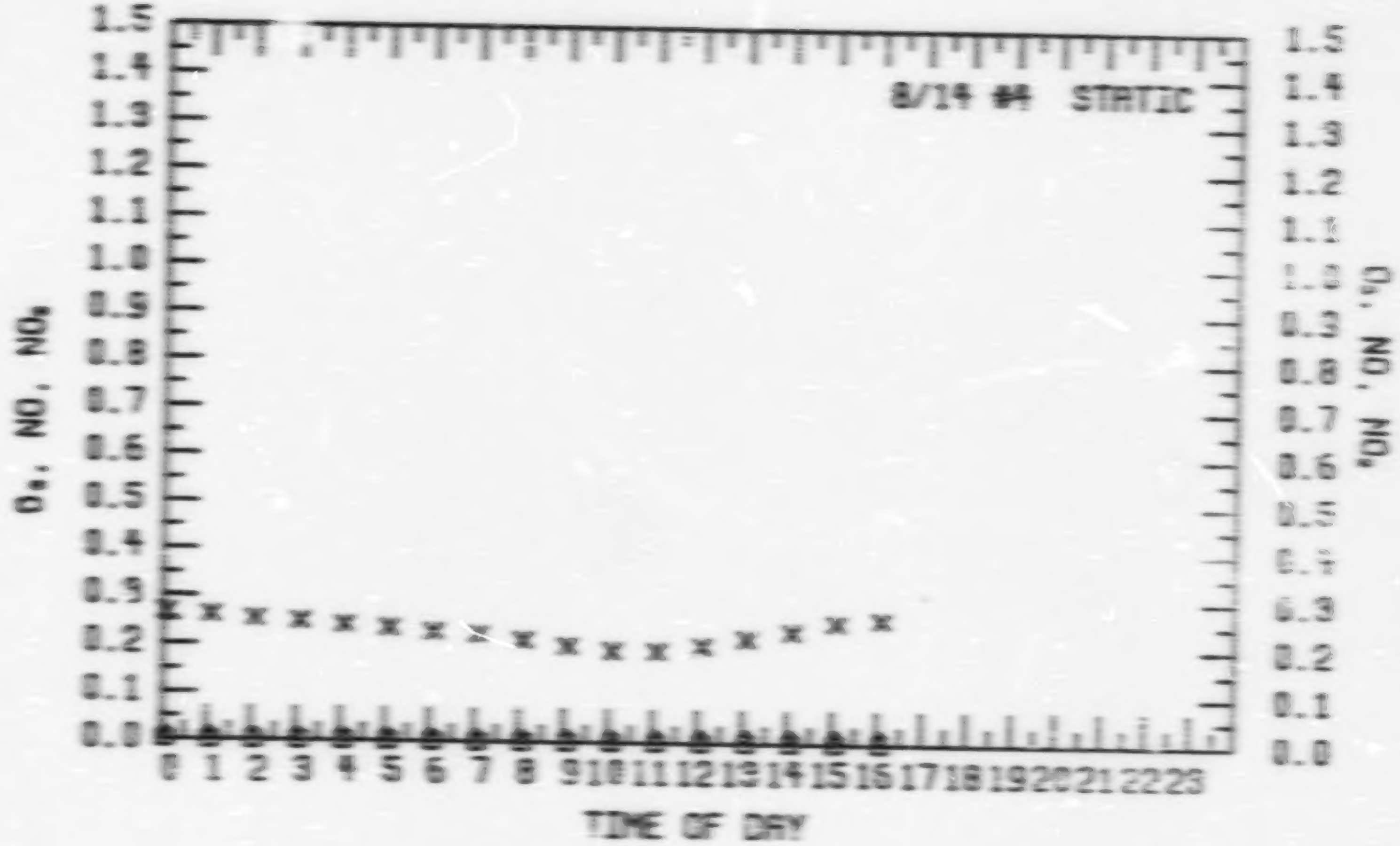
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


8/14 #4 STATIC
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1.2
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0.7
0.6
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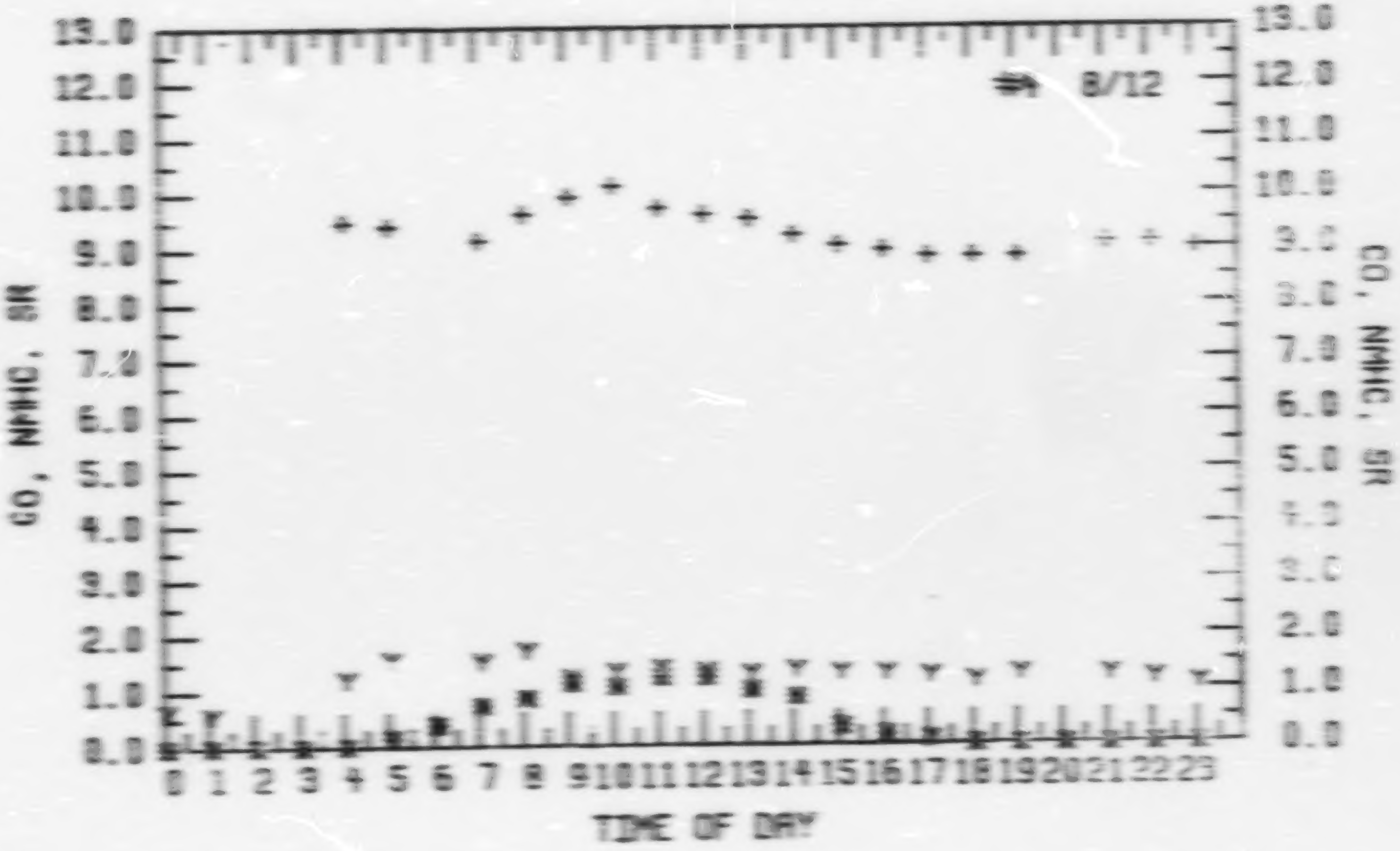
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY


#4 8/12
CO, NMHC, SR
TIME OF DAY
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5.0
6.0
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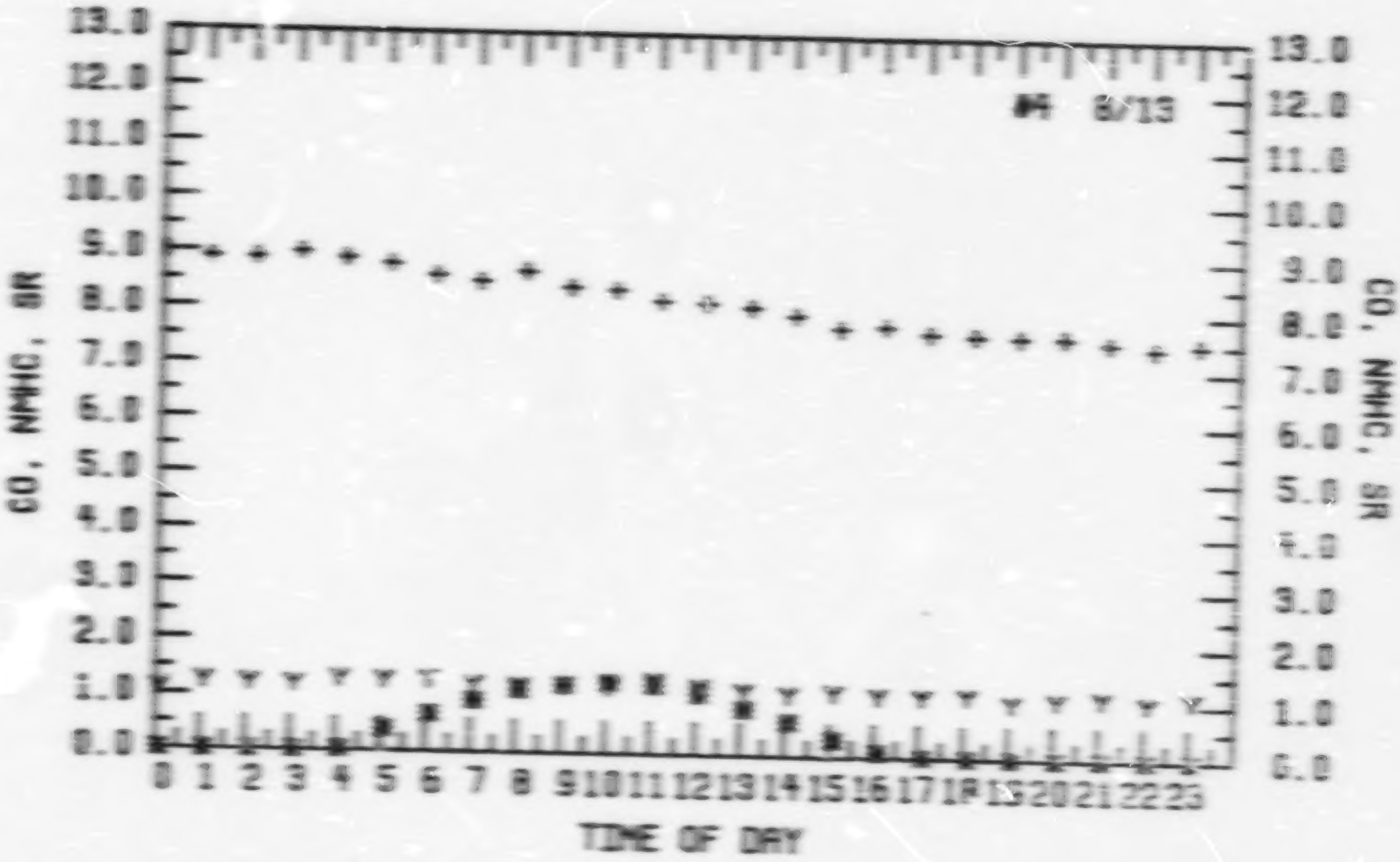
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23


#4 8/13
CO, NMHC, SR
CO, NMHC, SR
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7.0
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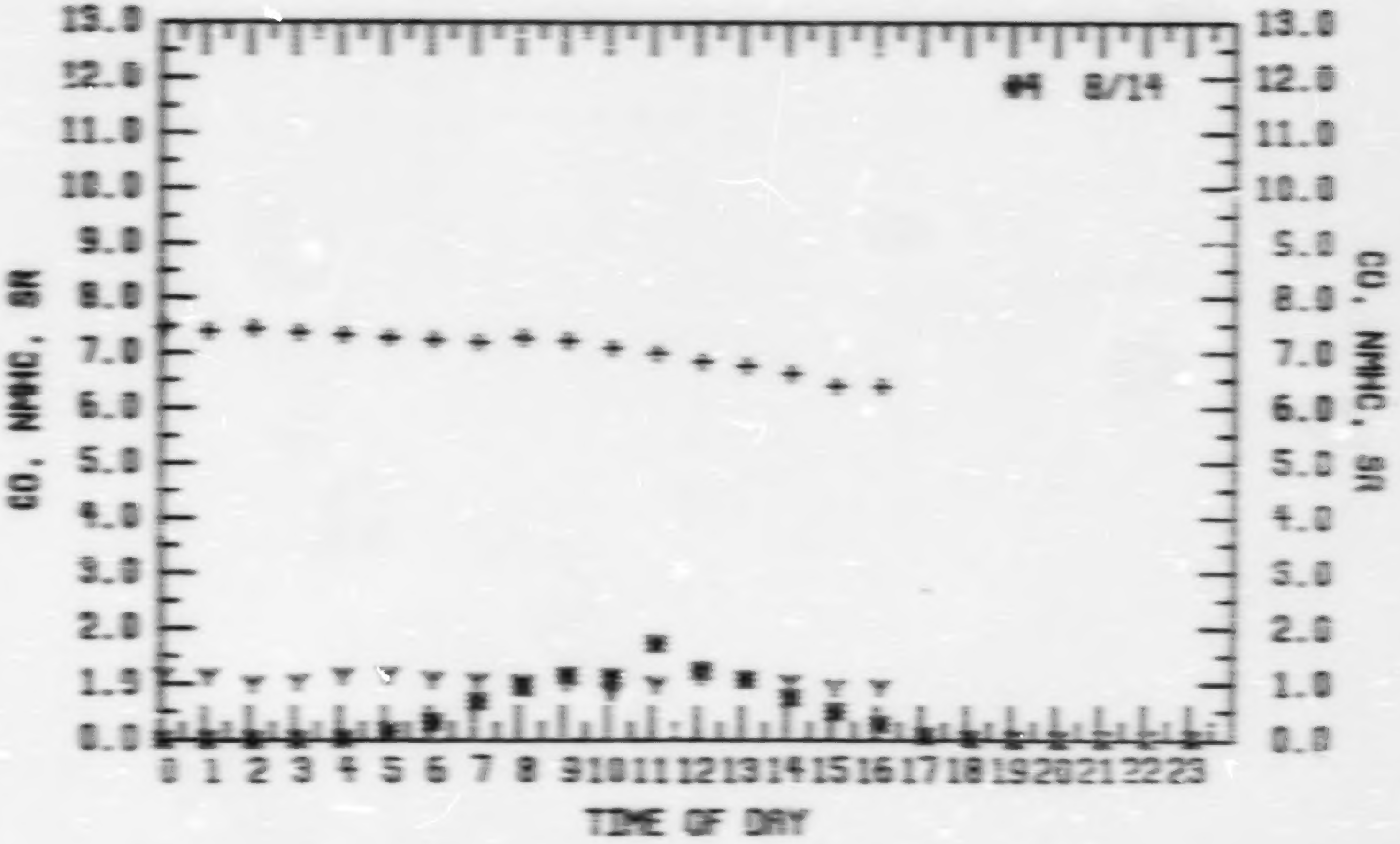
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY



#4 8/14
CO, NMHC, SR
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11.0
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
TIME OF DAY